

# Nanocrystal Structures

I. K. Robinson

University College London

Diamond Light Source

Course N1 – Nanomaterials and Nanosynthesis

Fuglsoecentret, Aarhus

# First UHV Experiments

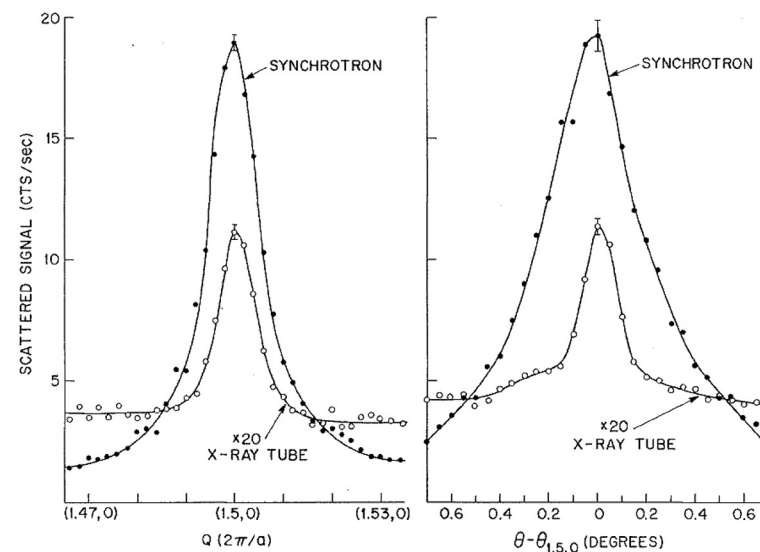
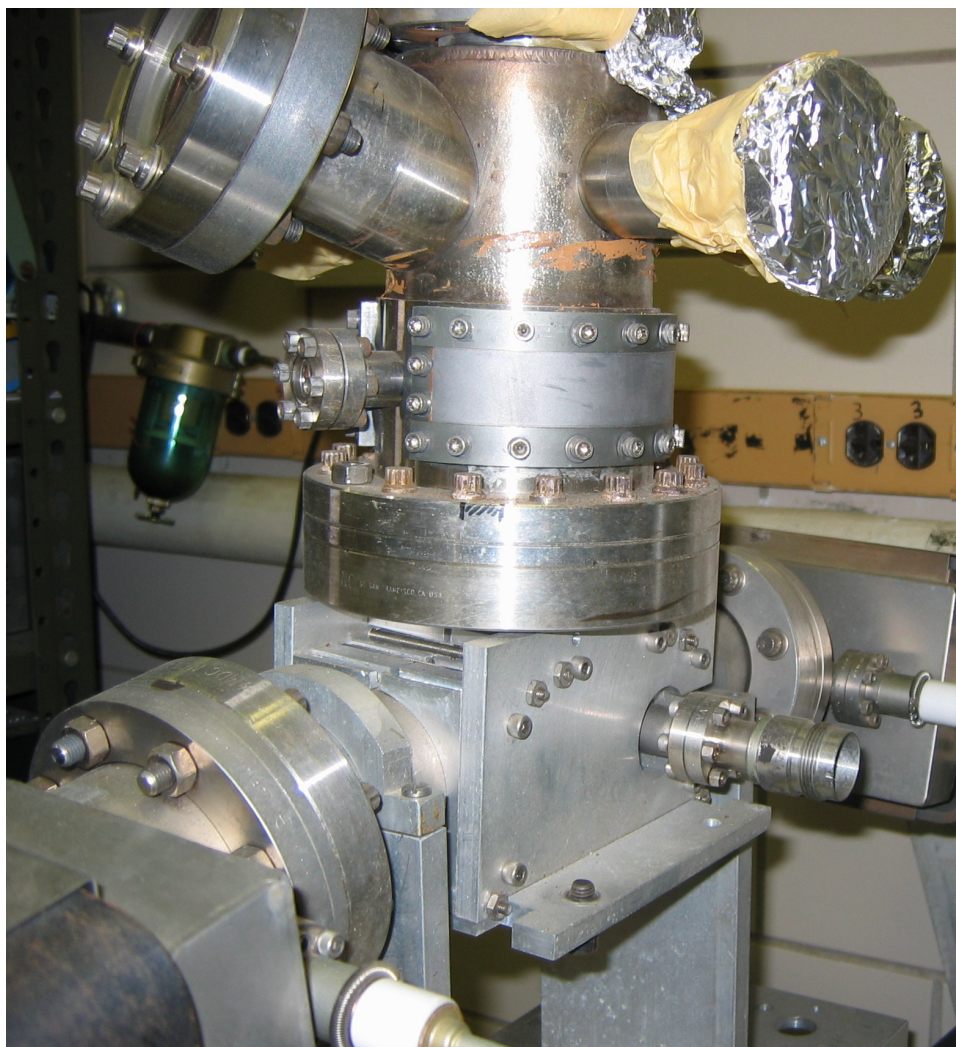
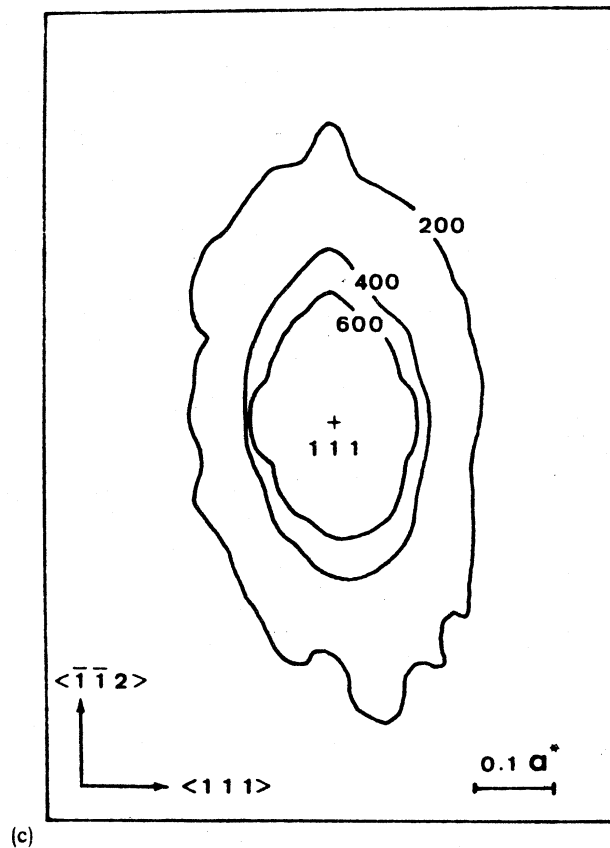


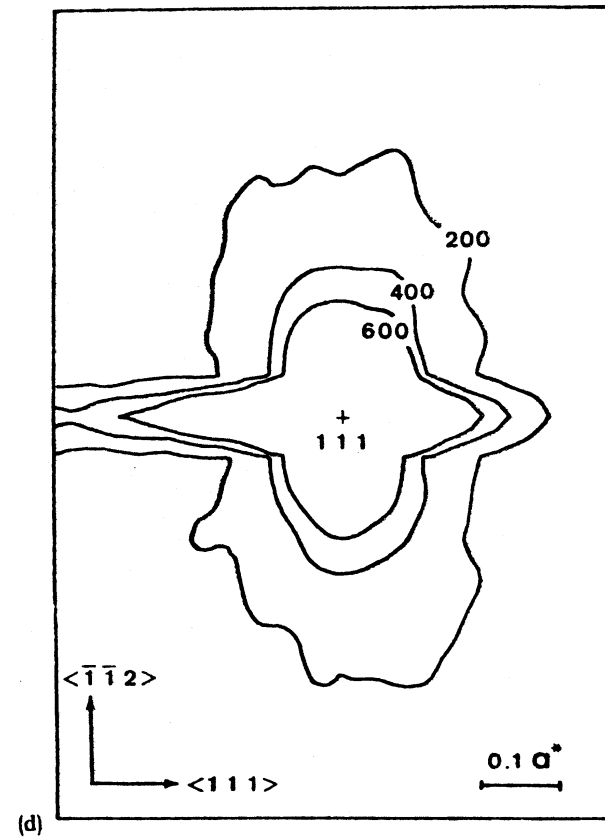
FIG. 1. A plot of the  $(\frac{3}{2}, 0)$  Bragg reflection as a function of the momentum transfer  $Q(2\pi/a)$  and the crystal's mosaic spread (deg).

P. Eisenberger and W. C. Marra,  
PRL 46 1081 (1981)  
experiments done at SSRL

# Diffuse Scattering from Si Wafer



(c) Unpolished wafer



(d) 40 microns removed

N. Kashiwagara, J. Harada and M. Ogino, J. Appl. Phys 54 2706 (1983)

# Powders of 2D Crystallites



FIG. 4. Microphotometer record of the diffract pattern of a heat treated carbon black, showing three-dimensional lattice reflections. Radiation  $\text{Cu } K\alpha = 1.539 \text{ \AA}$  monochromated by reflection from rocksalt.

Carbon black

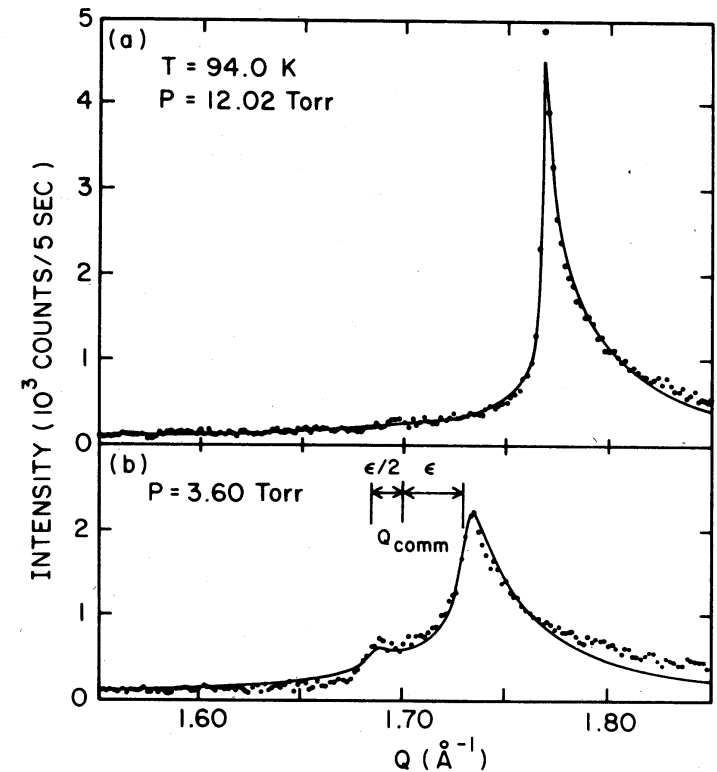
B. E. Warren, *Phys. Rev.* 59 693 (1941)

Kr on graphite

P. W. Stephens *et al*,

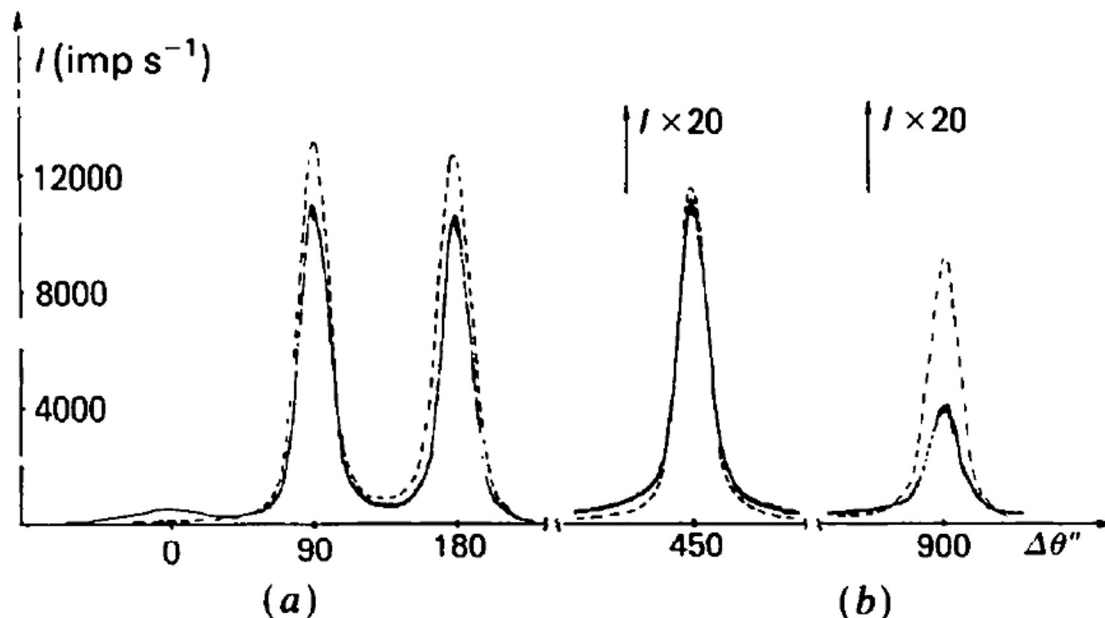
*Phys. Rev. B* 29

3512 (1984)



# Surfaces in Dynamical Diffraction

A. M. Afanas'ev *et. al.*, Acta Cryst A40 352 (1984)

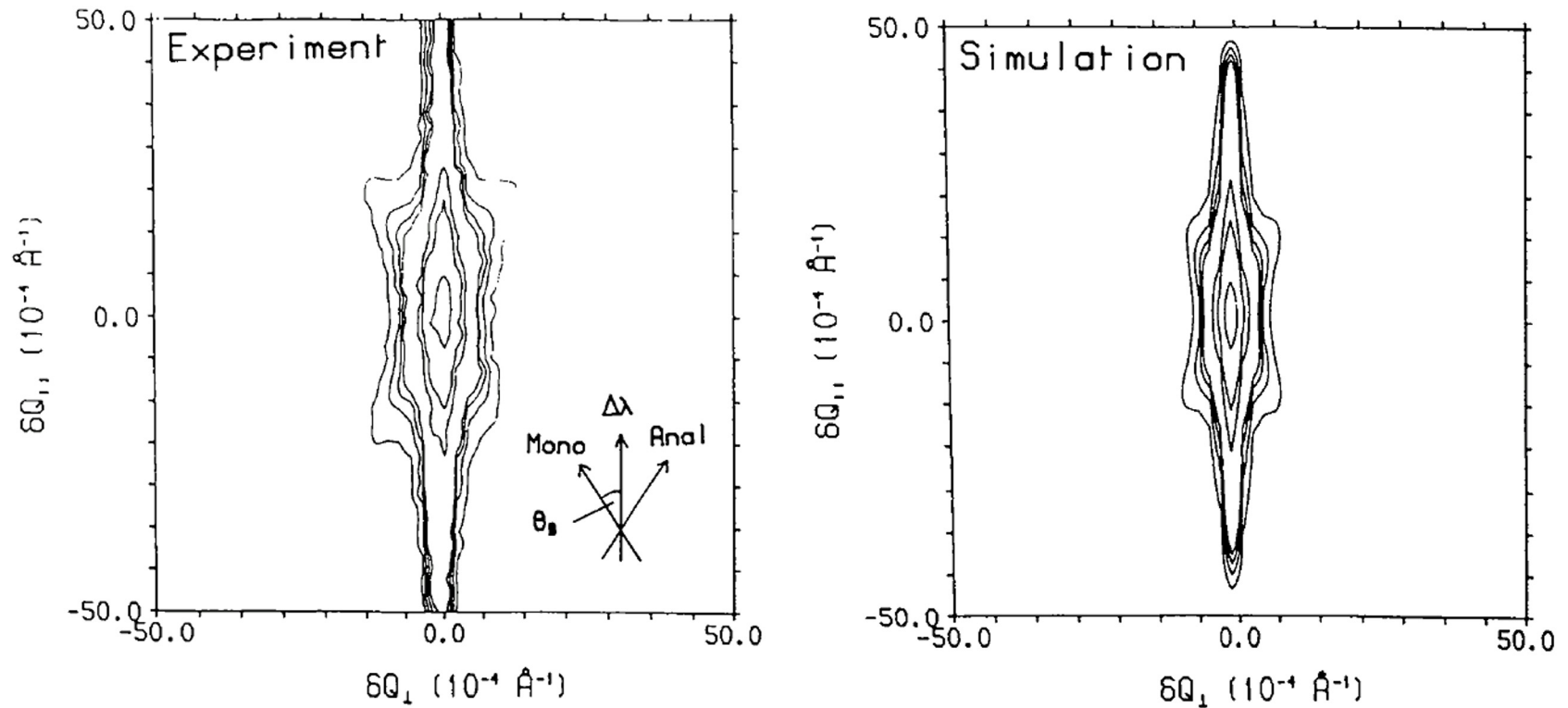


Effect of  
etching seen in  
triple-axis  
measurement of  
rocking curve

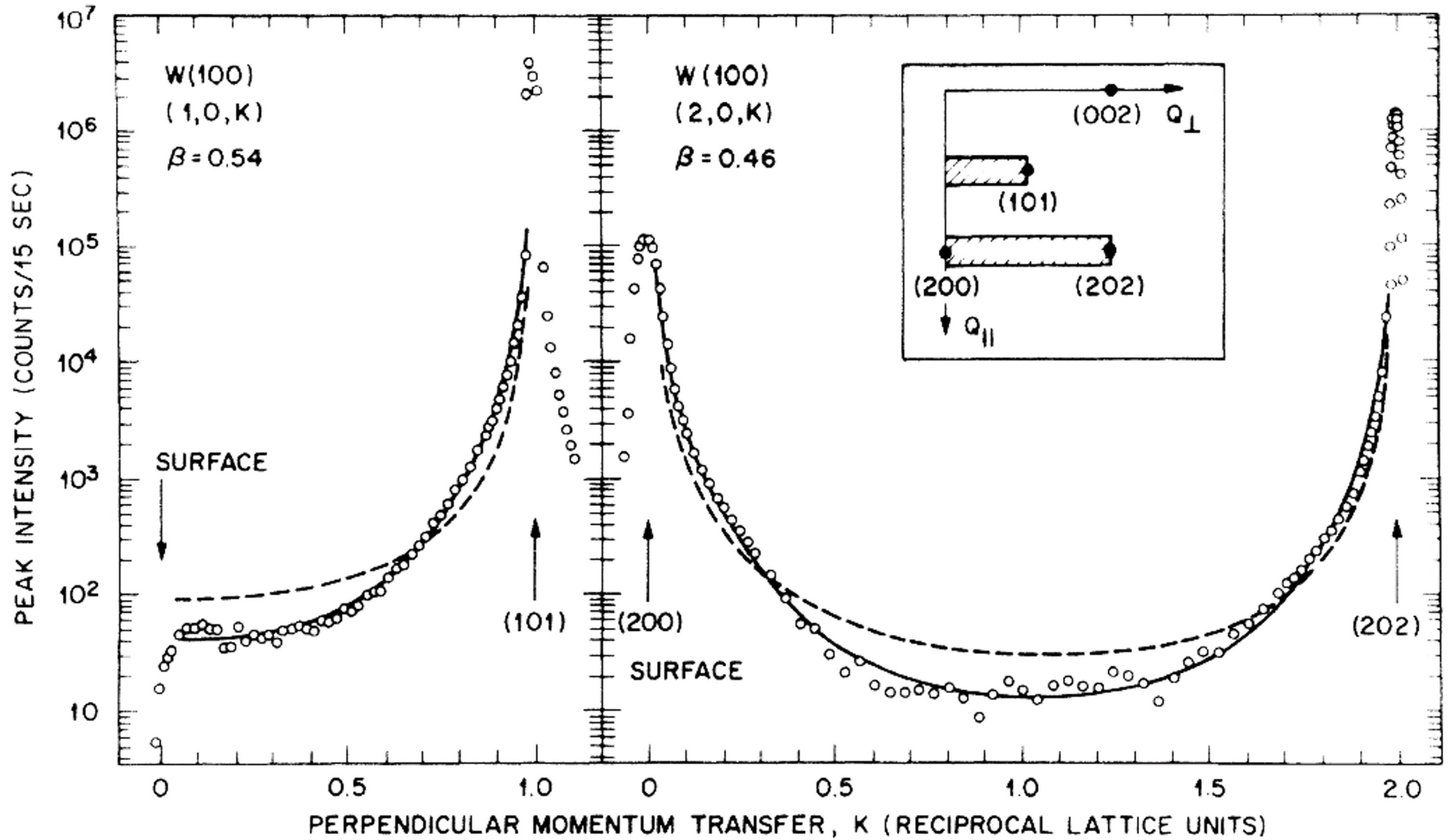
Fig. 2. TDC spectra from Ge(111) crystals,  $(n, -n, n)$  arrangement, symmetric Bragg diffraction for (a)  $\alpha = 90''$ , (b)  $\alpha = 450''$ . Dashed line for ideal crystal, solid line for crystal first polished with diamond paste and then partially etched.

# Resolution Function of the Triple-Axis Spectrometer

R. A. Cowley *et. al.*, Acta Cryst A45 415 (1989)



# CRYSTAL TRUNCATION RODS AND SURFACE ROUGHNESS



# Diffraction as a Surface Integral

**Die äußere Form der Kristalle  
in ihrem Einfluß auf die Interferenzerscheinungen  
an Raumgittern**

**Von M. v. Laue**

Annalen der Physik [5] 26 55 (1936)

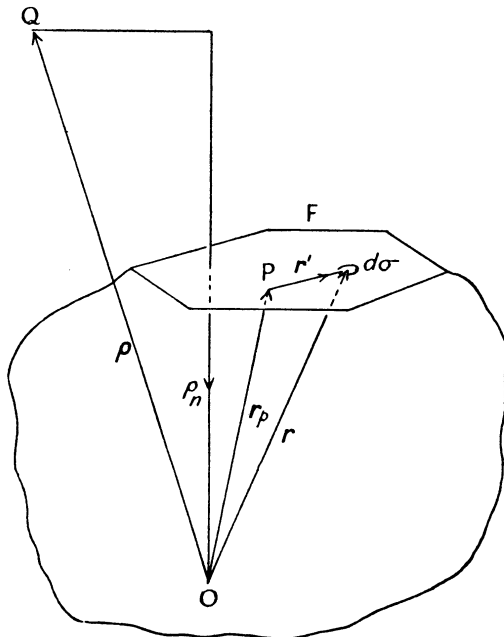
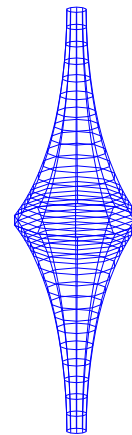
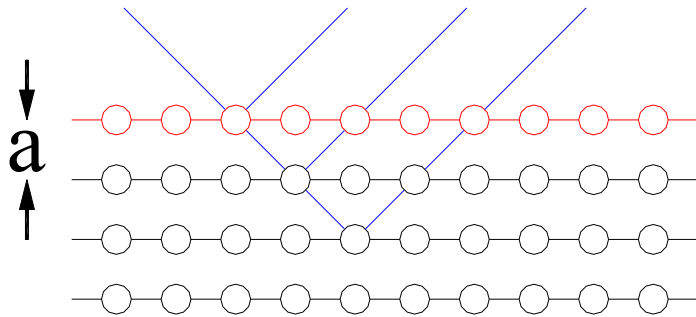


FIG. 200

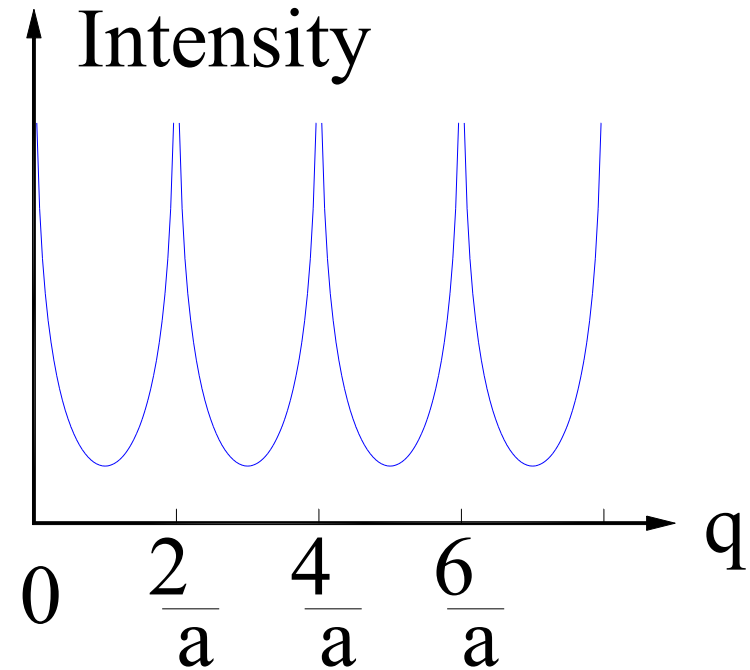


“Stacheln”

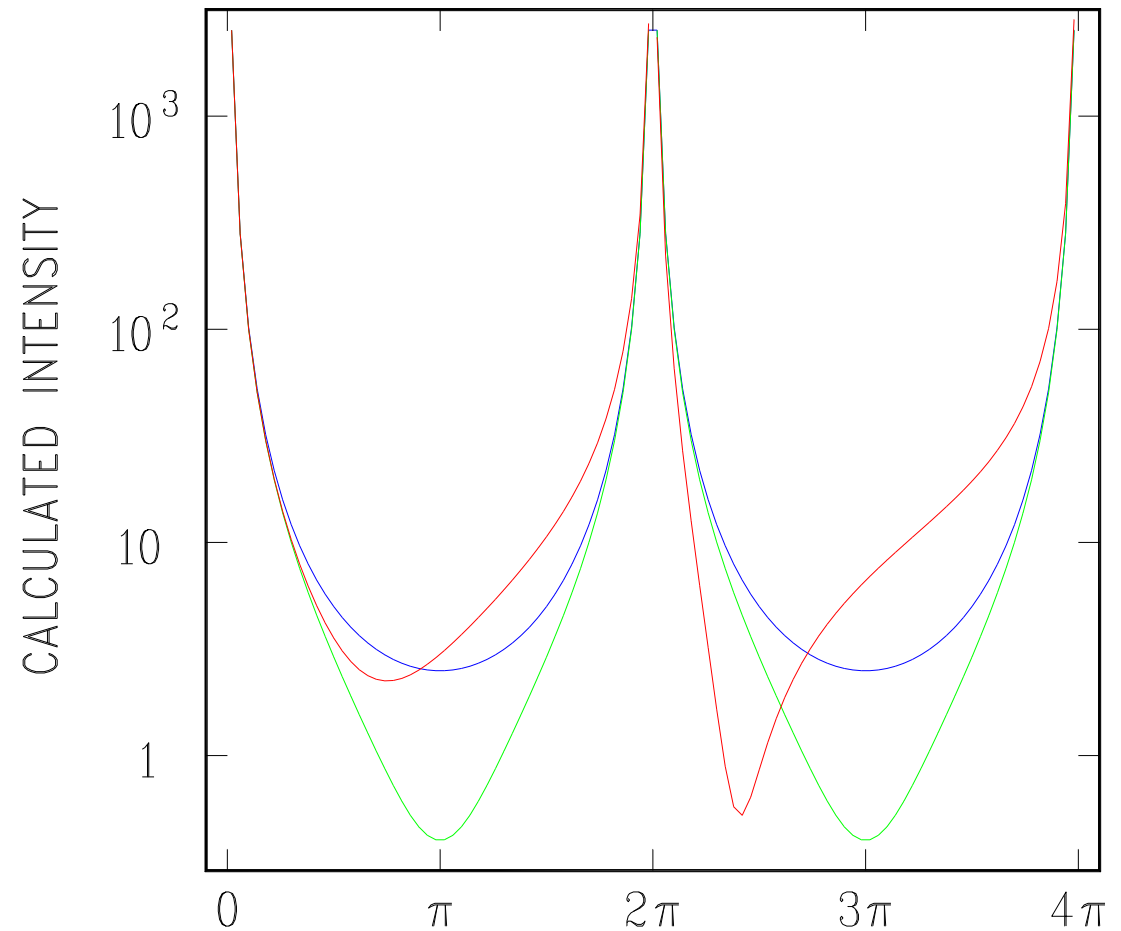
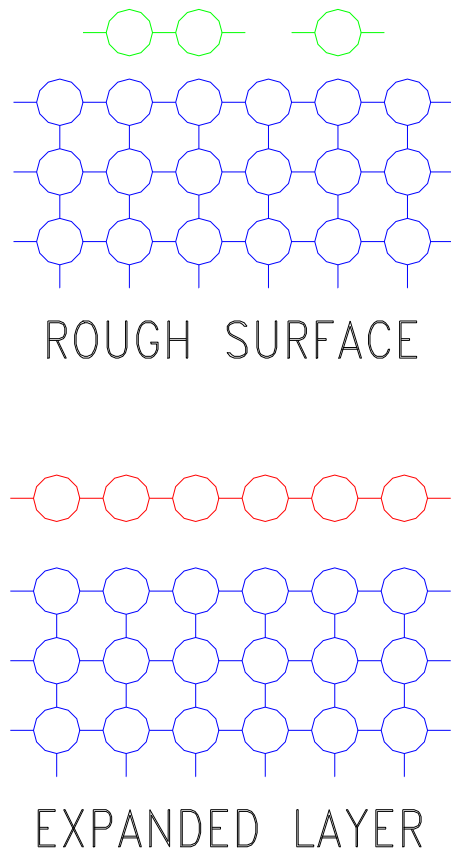
# Origin of Truncation Rods



$$\begin{aligned} F_{CTR} &= \sum_{n=0}^{\infty} A_n \\ &= \sum_{n=0}^{\infty} f_L e^{inqa} \\ &= \frac{f_L}{1 - e^{iqa}} \end{aligned}$$

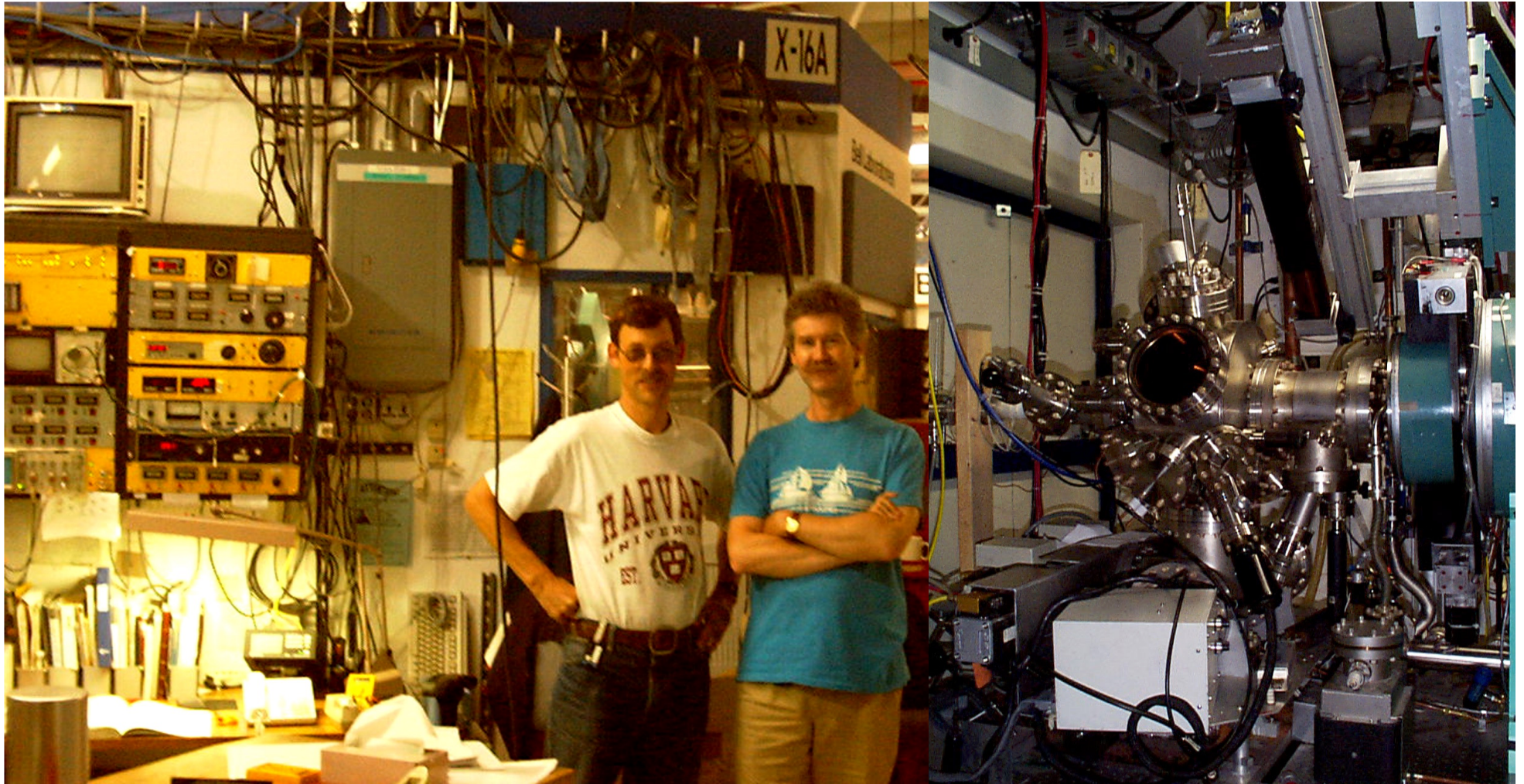


# CTR is Sensitive to Surface Structure

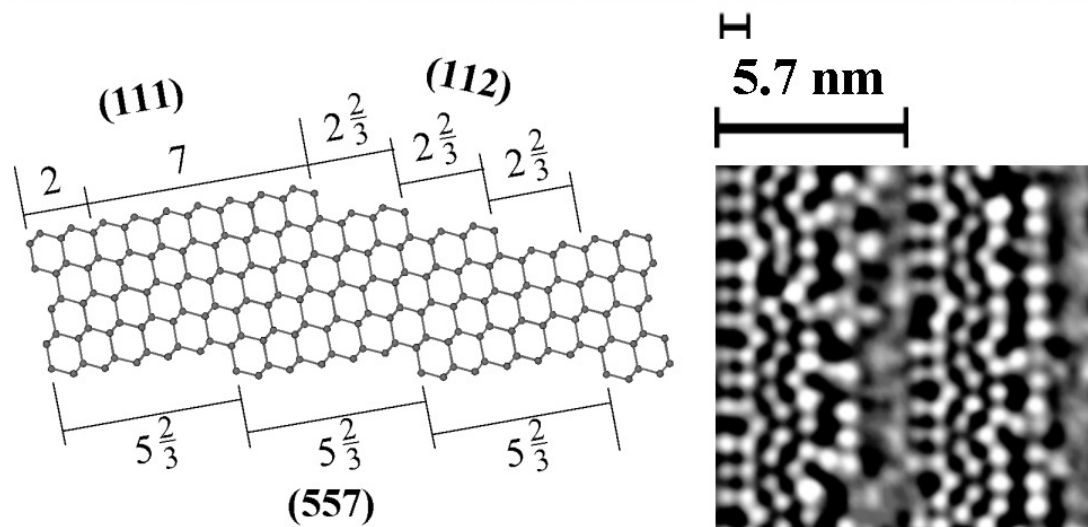
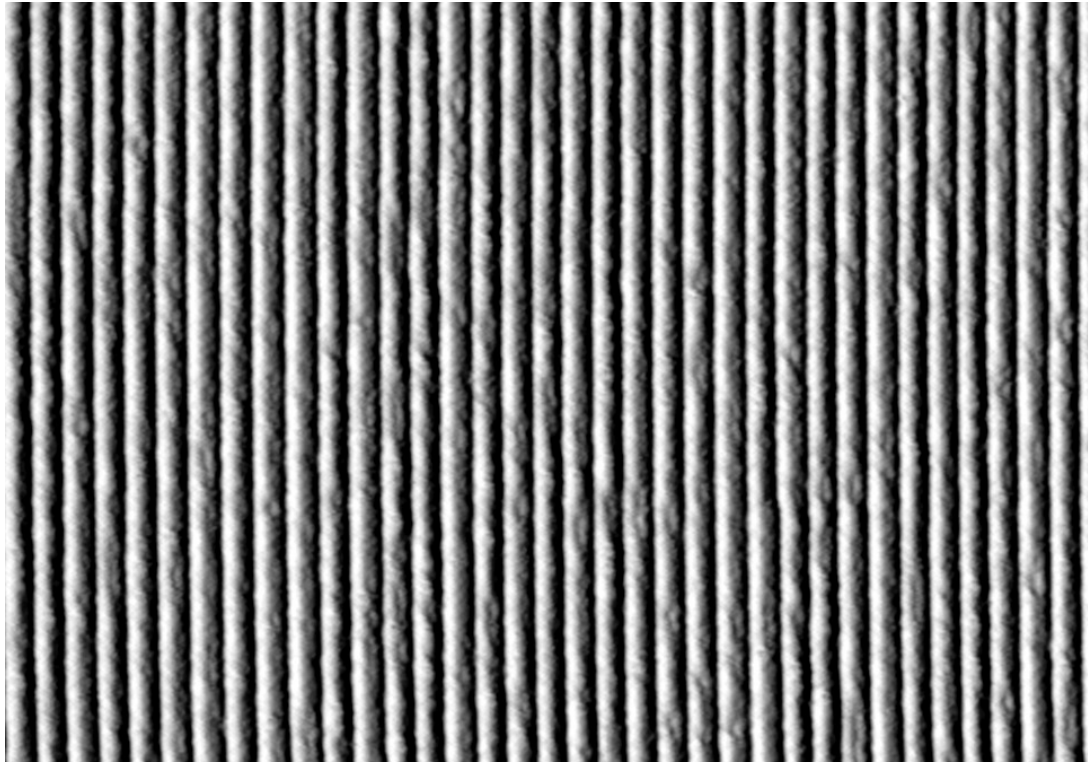


# X16A Surface X-ray Diffraction

operating since 1987 ...



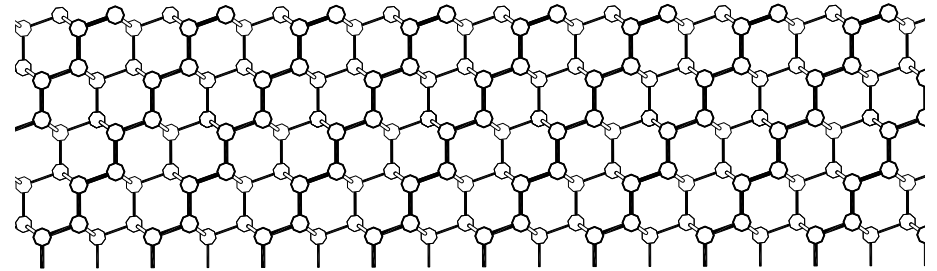
I. K. Robinson iNANO School



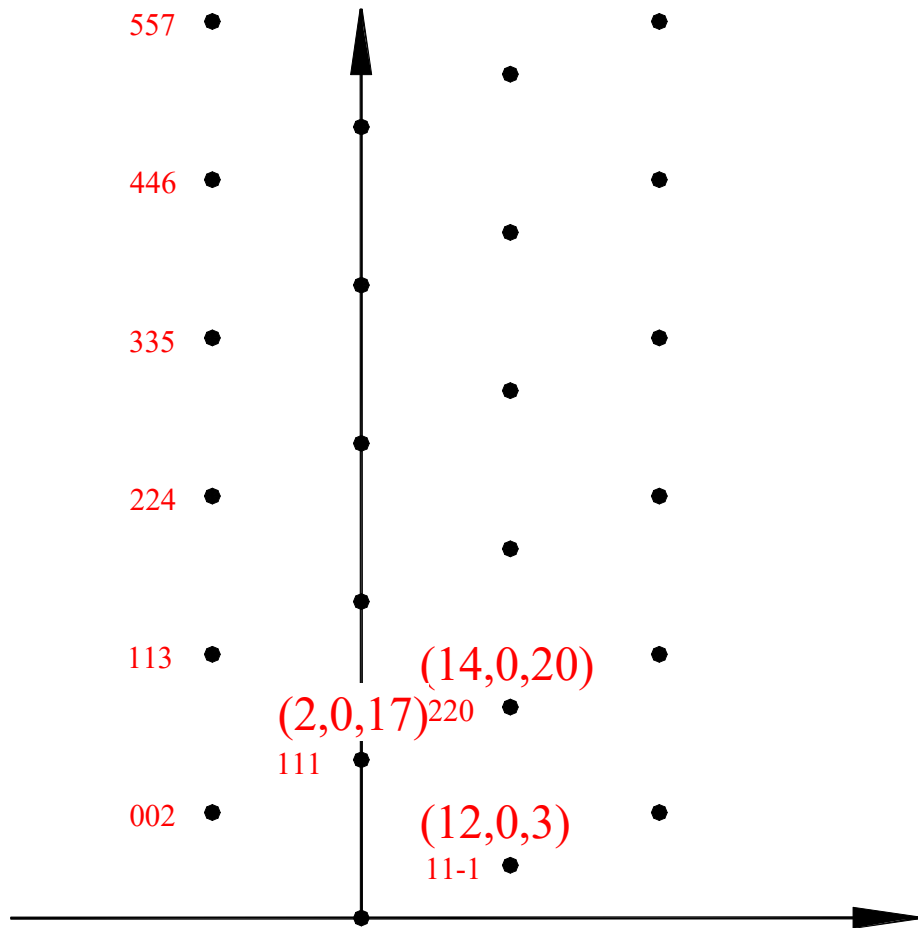
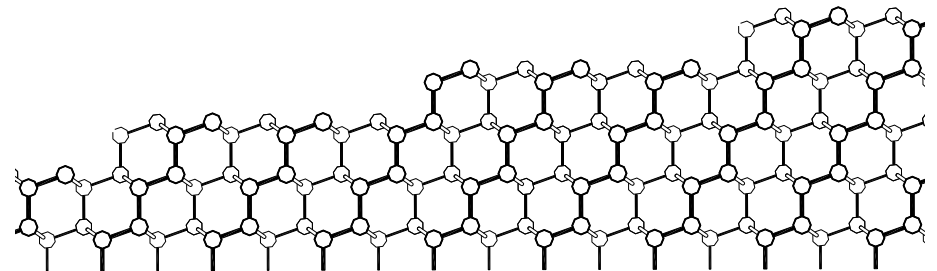
I. K. Robinson iNANO School

# Crystallography of Stepped Surfaces

Silicon (111)



Si(557) surface



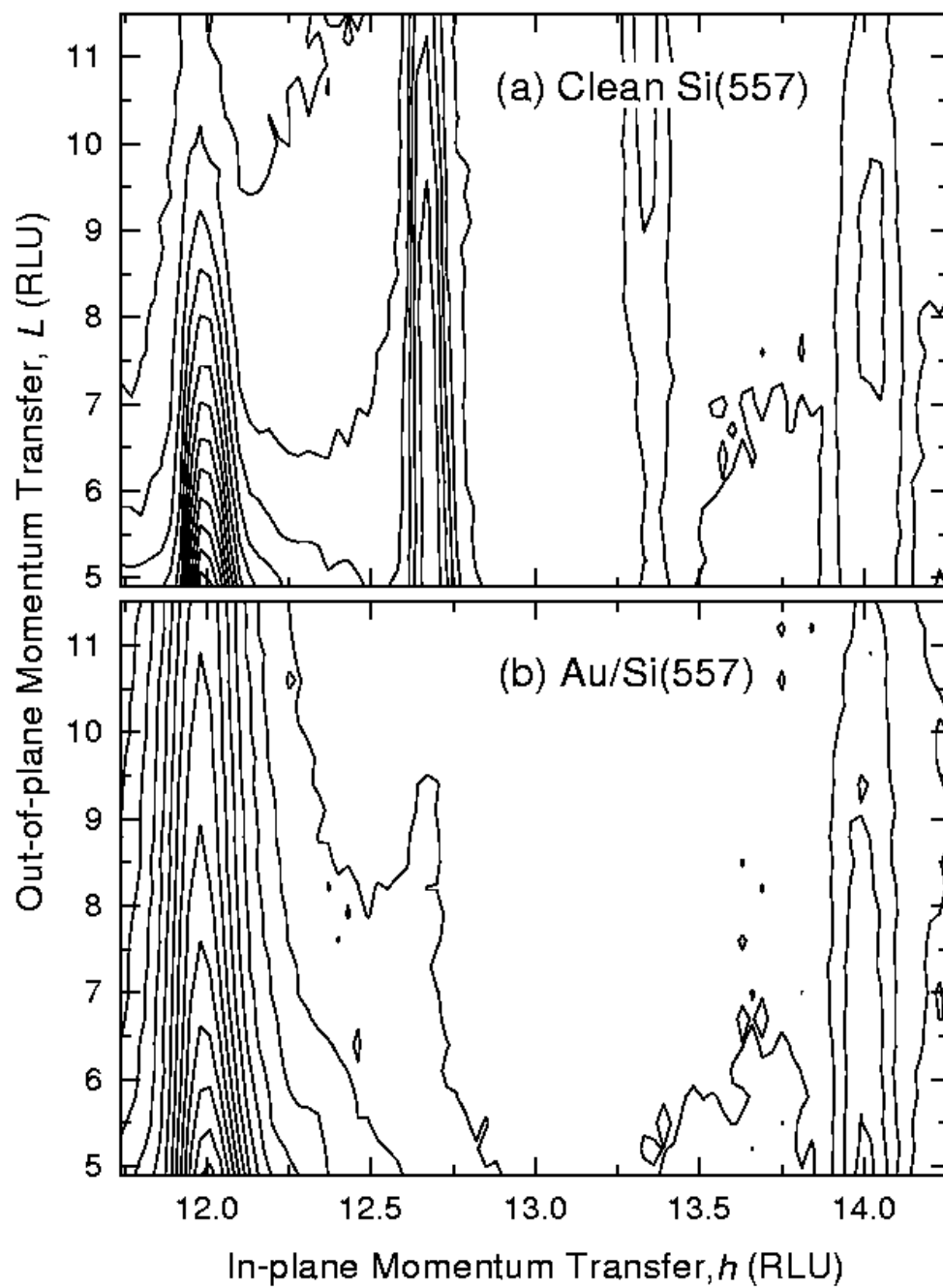
# Alignment is Straightforward

CALCULATED PARAMETERS:

	A	B	C	ALFA	BETA	GAMMA				
REC:	0.164431	1.63392	0.116412	90.06	90.03	89.93				
DIR:	38.2118	3.84548	53.9736	89.94	89.97	90.07				
	H	K	L	TTH	TH	PHI	CHI	ALP	CTS	ERROR
OR 1 =	12.0	0.0	3.0	21.938	112.920	50.308	-1.137	3.841	22456	0.0027
OR 2 =	-5.0	1.0	7.0	20.284	97.018	307.482	-2.259	9.179	20719	0.0018
OR 3 =	14.0	0.0	20.0	26.411	113.142	40.844	-1.290	26.483	13639	0.0009
OR 4 =	12.0	2.0	3.0	43.135	110.470	4.520	-2.092	4.313	12772	0.0009

Lambda = 1.20913 Å,  $wv = 5.19647$ , Energy = 10.2542 keV (FIXED)  
Five-Circle Mode using alm = 2 and bem = 2:

Centered Orthorhombic unit cell contains two steps.



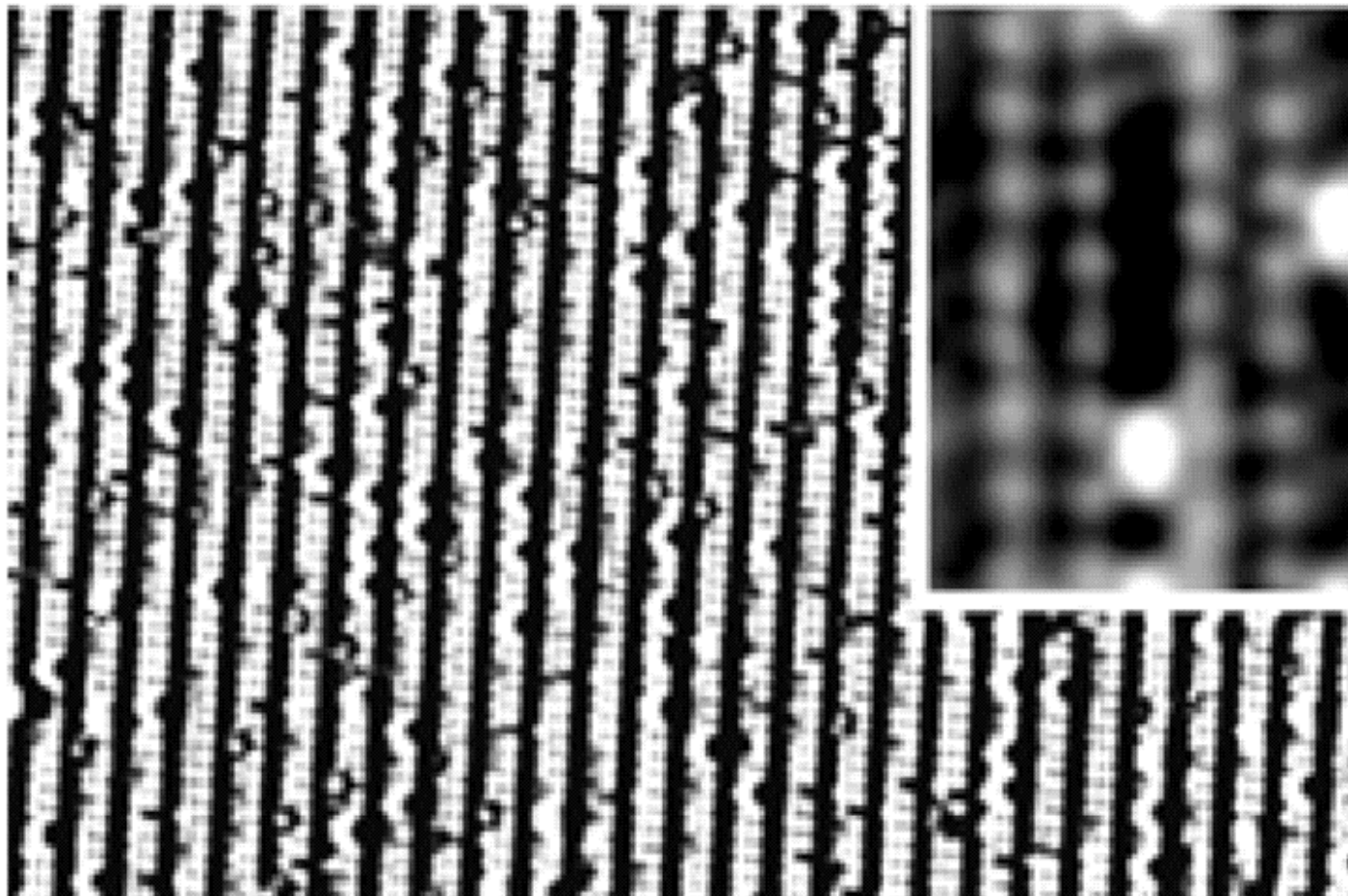
$3 \times 1$  clean  
surface

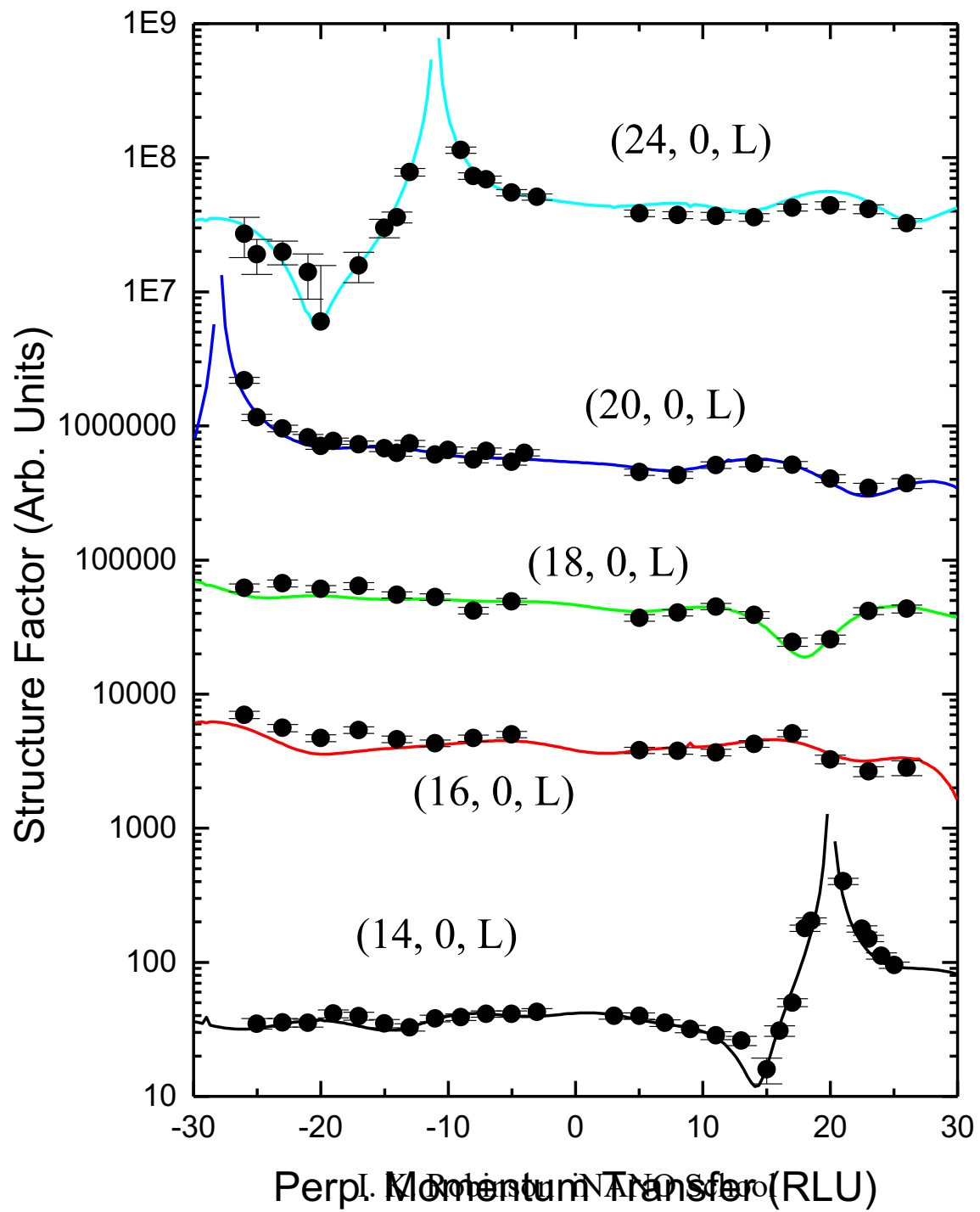
$1 \times 1$  surface  
with 0.2ML Au  
at 600C

# STM of Si(557)/Au

R. Losio, et. al., Phys. Rev. Lett. 86 4632 (2001)

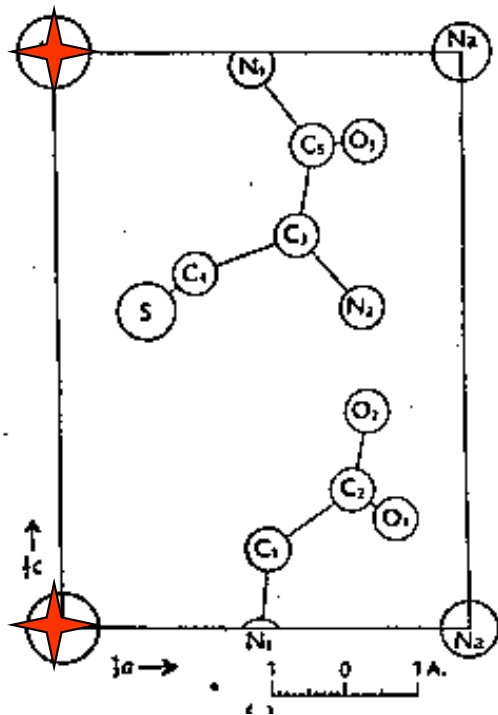
1.9 nm



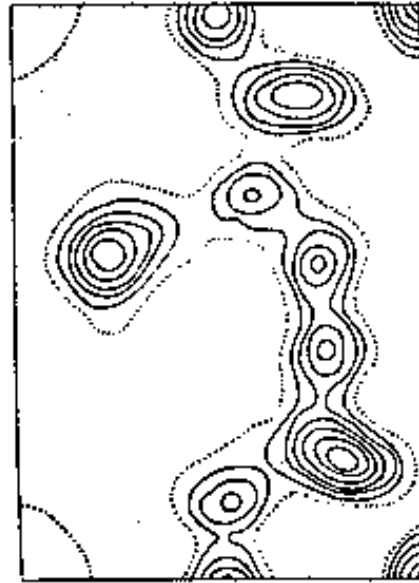


# Phasing by a Single Heavy Atom

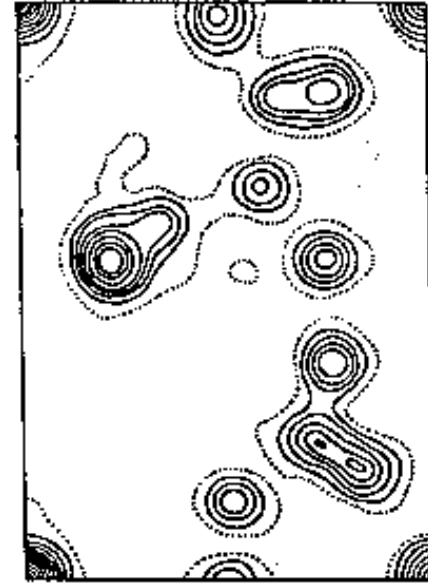
H. B. Dyer, Acta Cryst. 4 42 (1951)



Cysteinylglycine  
sodium iodide

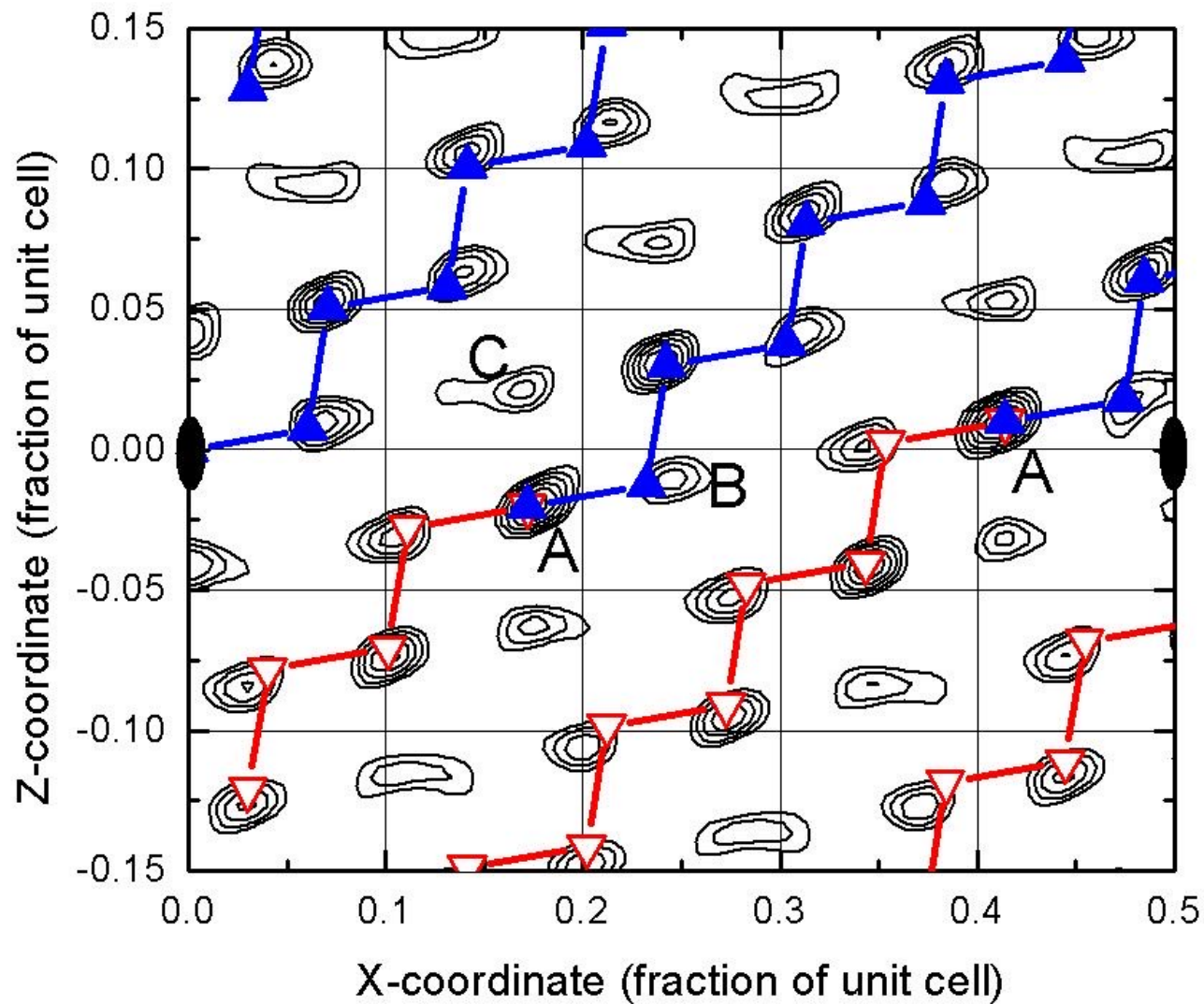


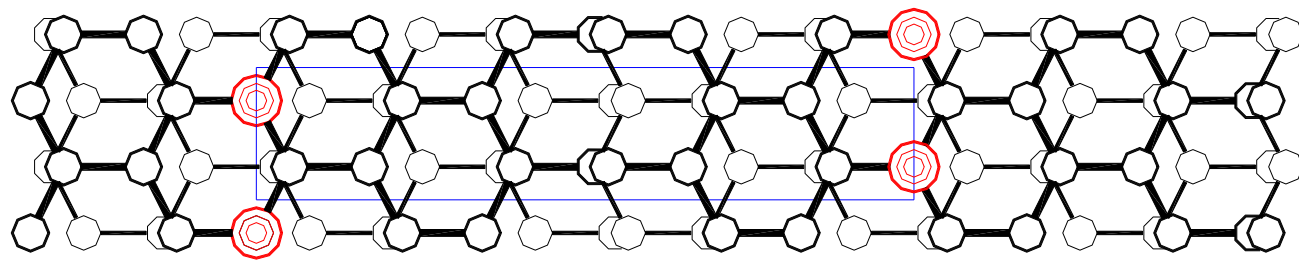
Patterson



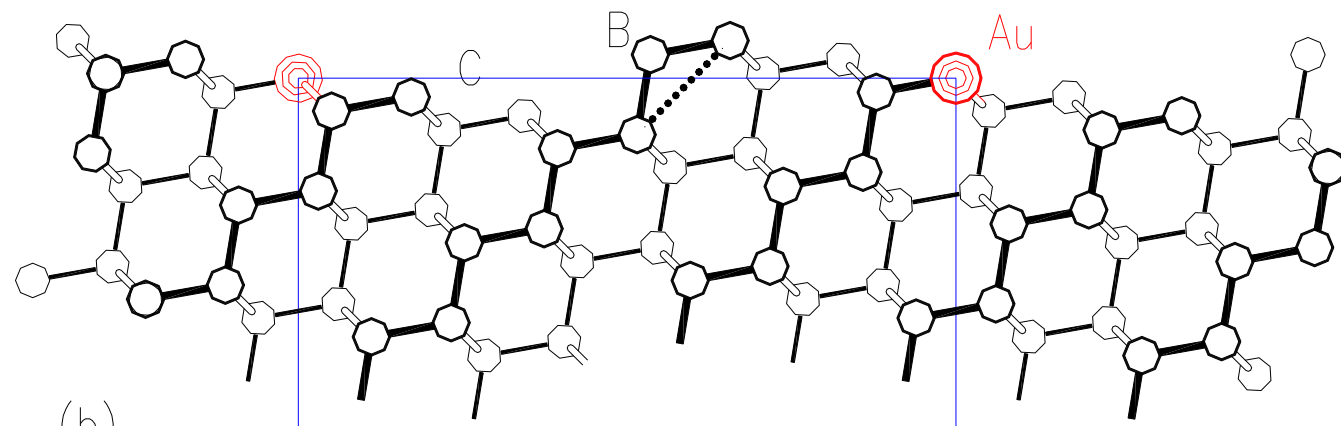
Electron density

# X-Z Patterson of Au/Si(557)

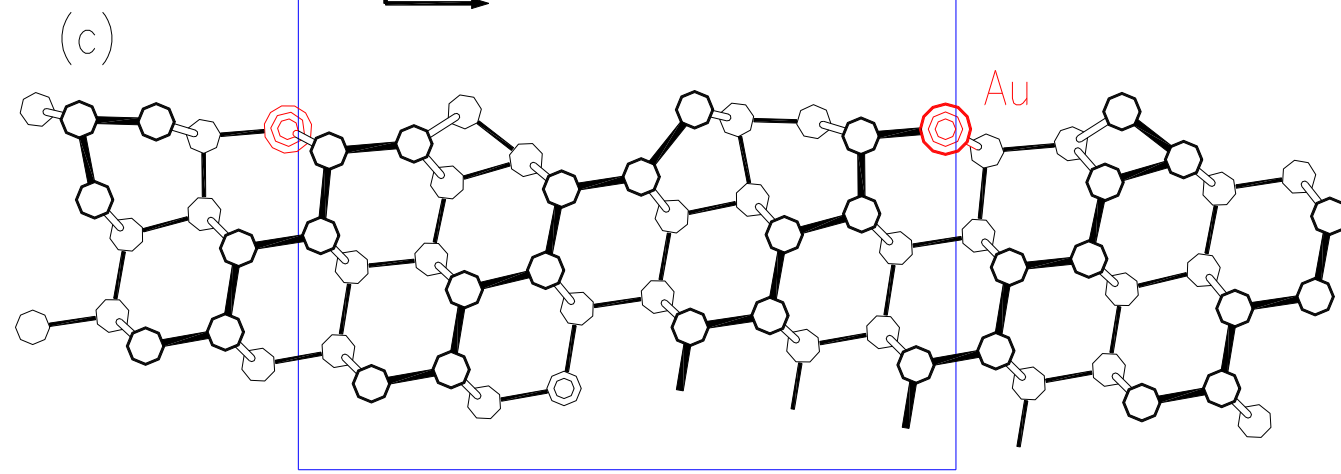




(a) A coordinate system with a vertical y-axis and a horizontal x-axis.

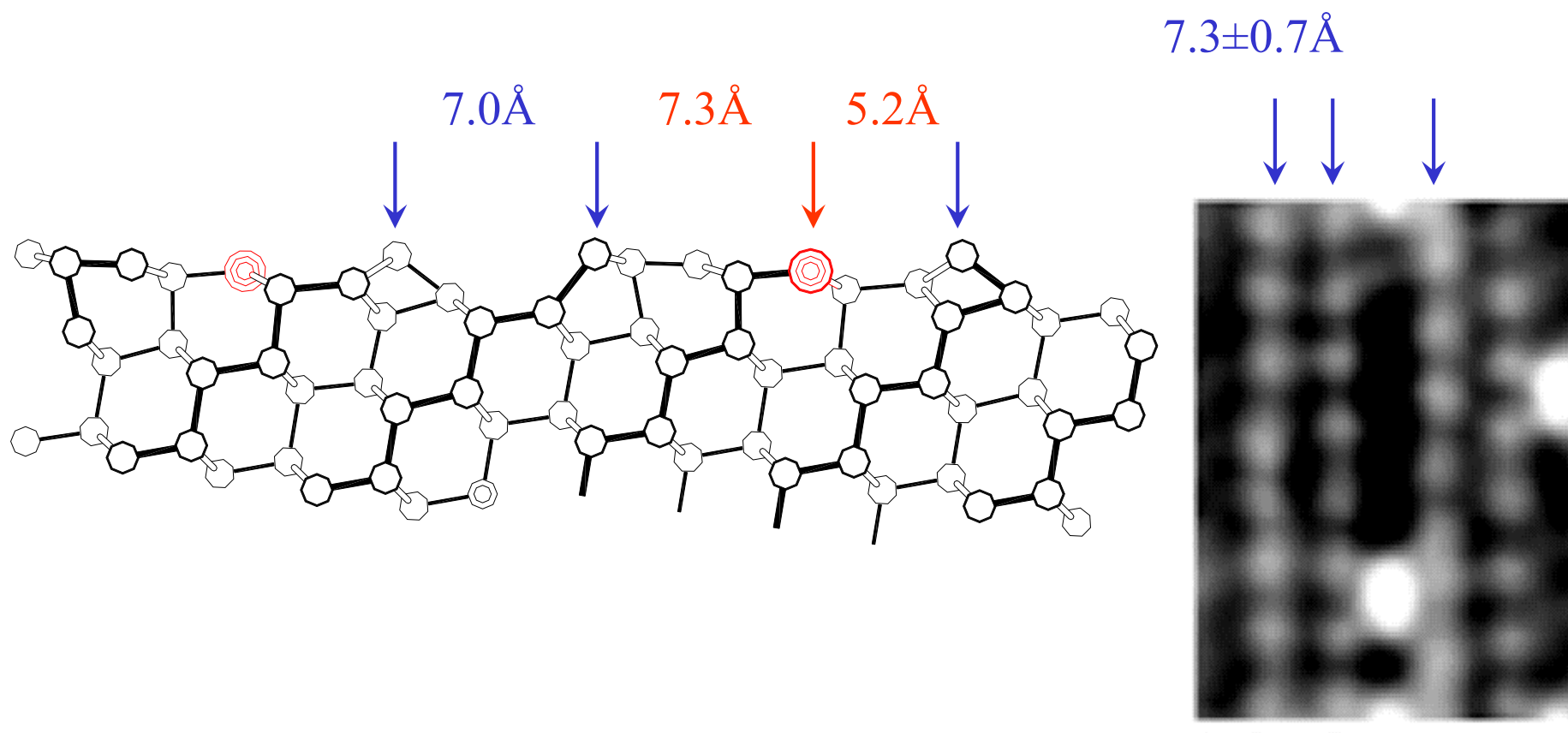


(b) A coordinate system with a vertical z-axis and a horizontal x-axis.



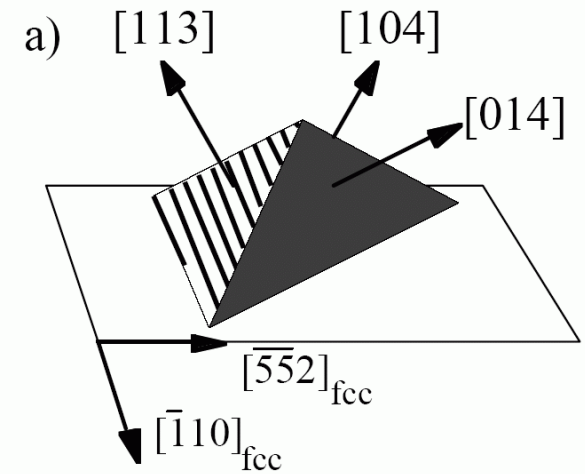
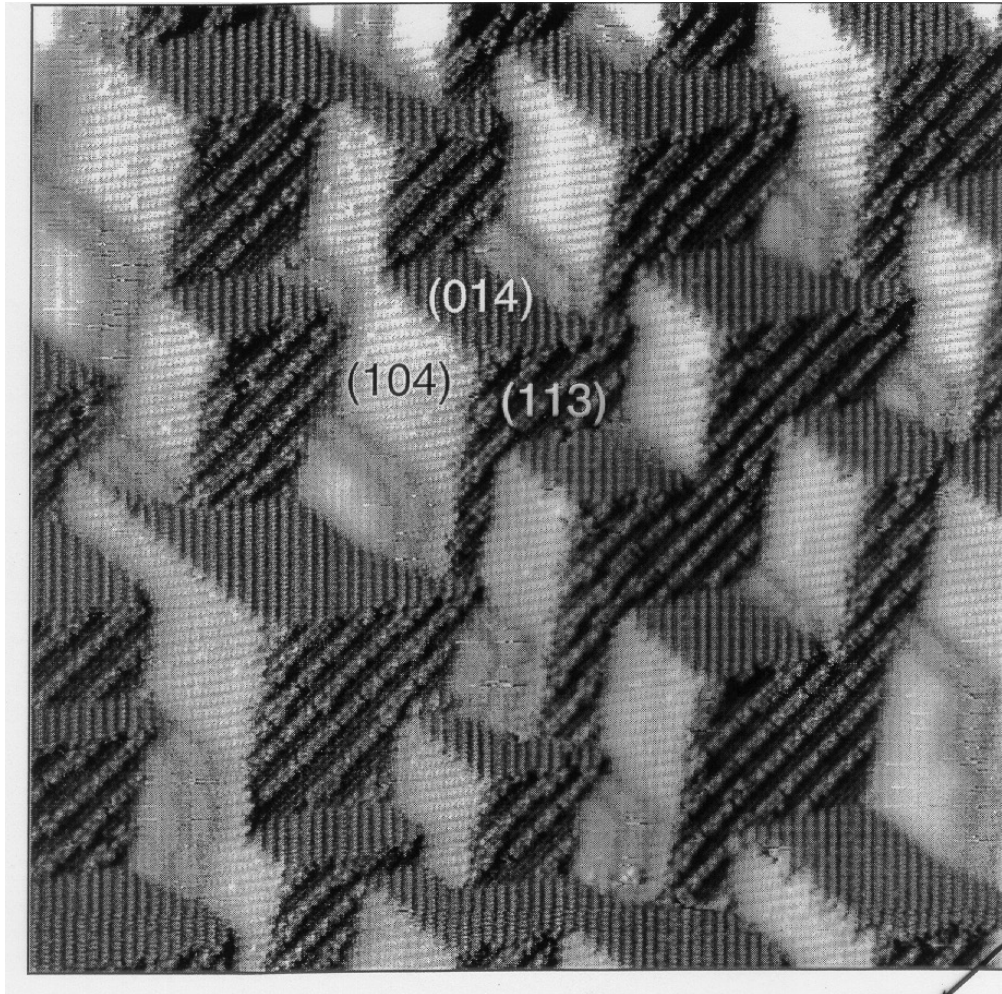
(c)

# Comparison with STM



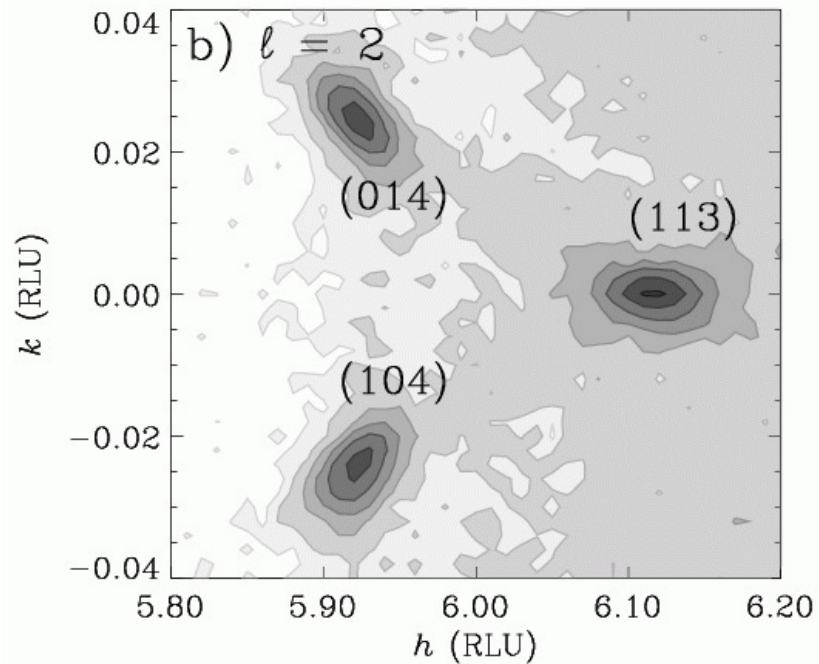
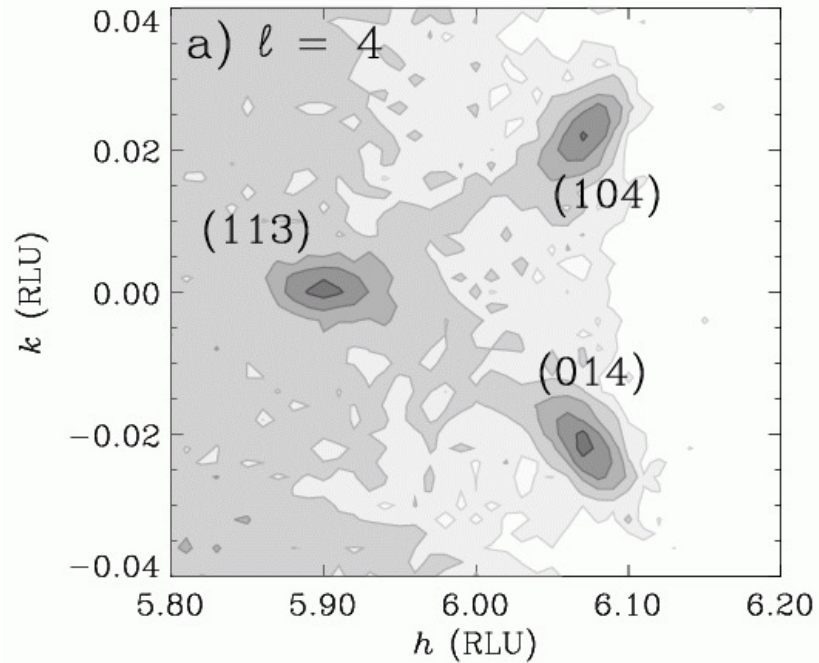
# Cu(115) after Oxidation: STM

S. Reiter and E. Taglauer, Surf. Sci. 367 33 (1996)

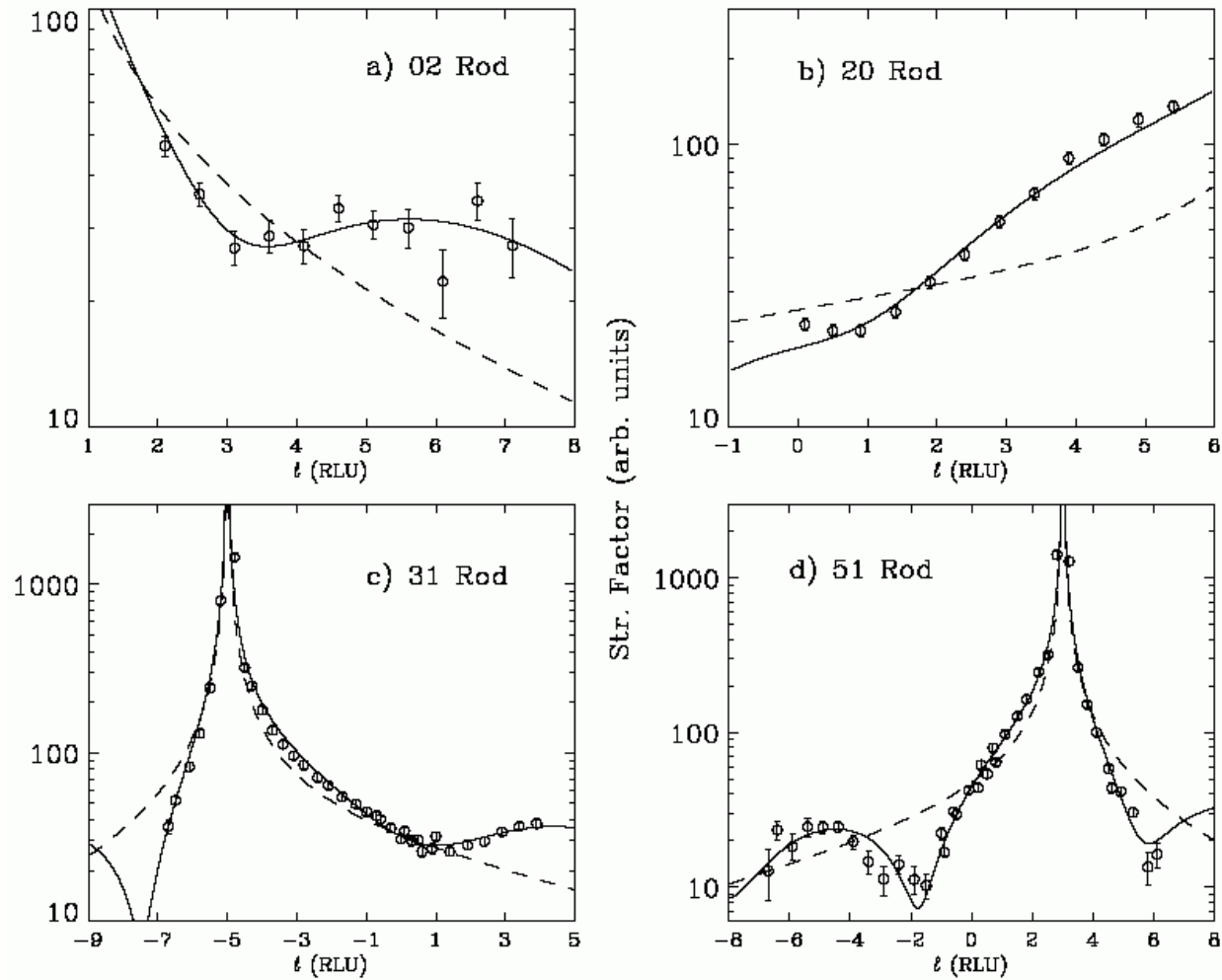


# Cu(115) after Oxidation: X16A

Don Walko, UIUC PhD  
Dissertation (2000)



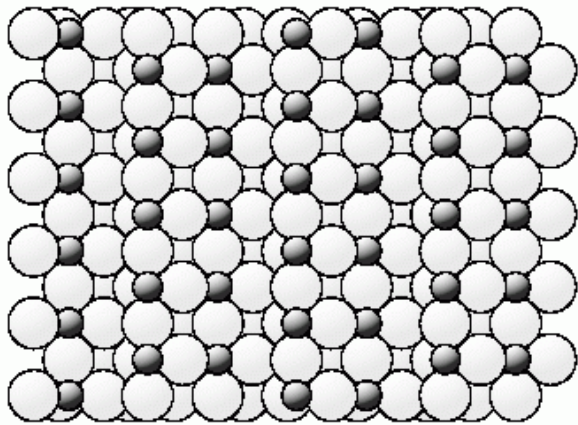
# Re-index CTRs for Cu(104) facets



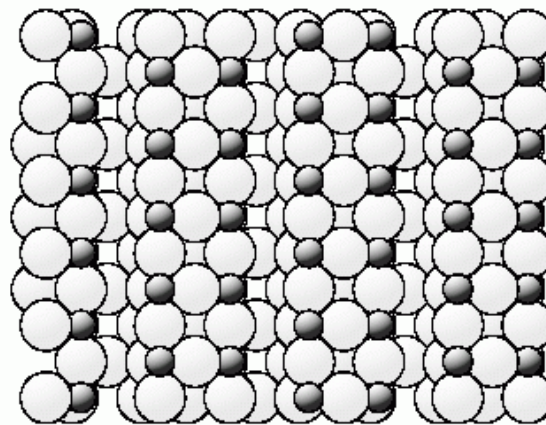
# Surface Structures of Cu(104)-O

E. Vlieg, S. M. Driver, P. Goettkindt, P. J. Knight, W. Liu, J. Luedecke, K. A. Mitchell, V. Murashov, I. K. Robinson, S. A. de Vries and D. P. Woodruff, *Surface Science* **516** 16-32 (2002)

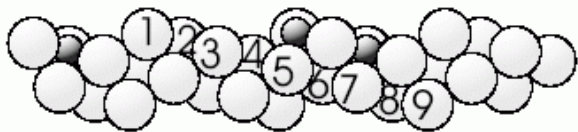
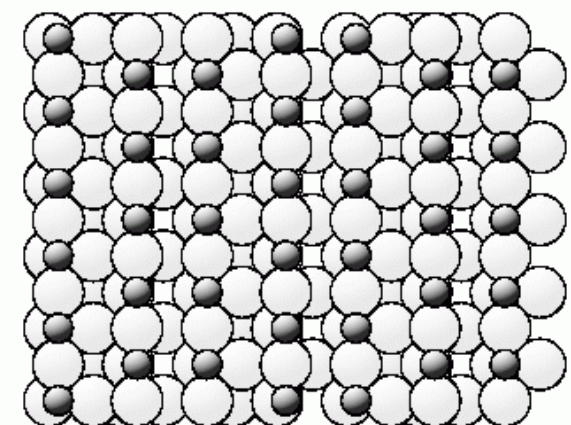
Overlayer



Missing Row 4



Missing Row 2



Perderau and Rhead



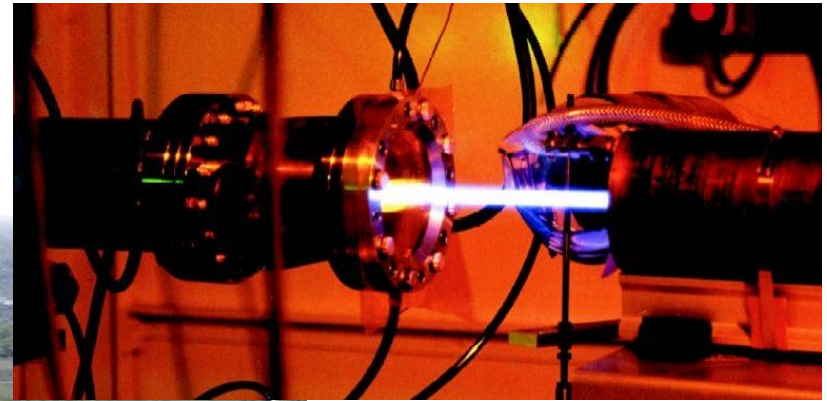
Robinson et al



Woodruff et al

# Synchrotron Radiation

Urbana



34-ID-C



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# Diamond Light Source (RAL)



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# Last Girder – March 2006



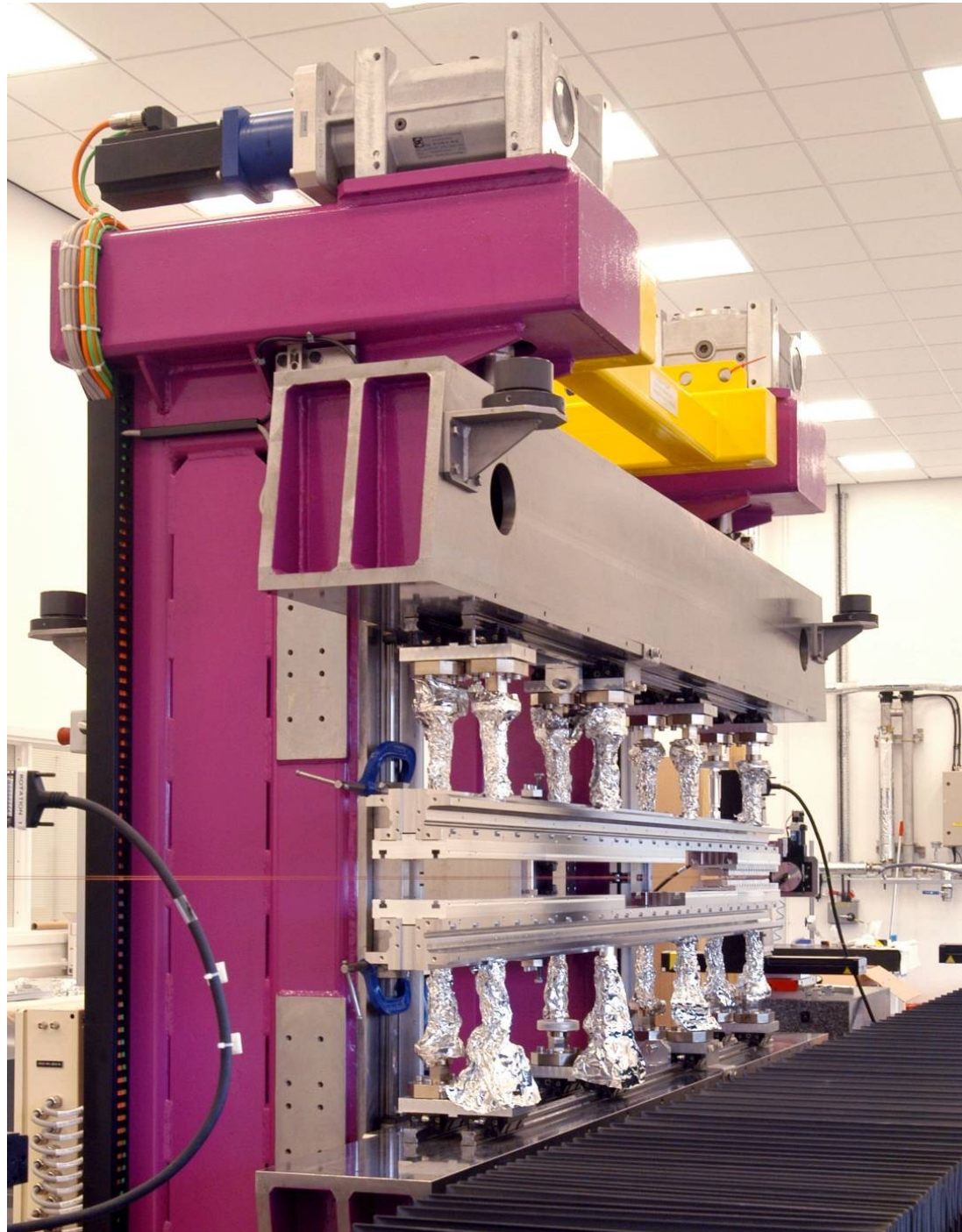
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# Typical beamline: I-22

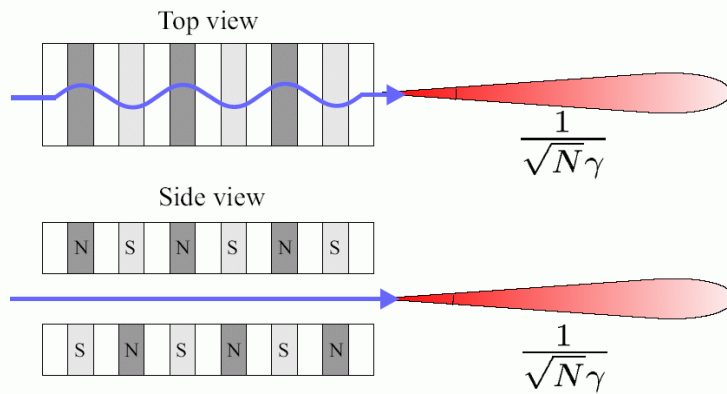


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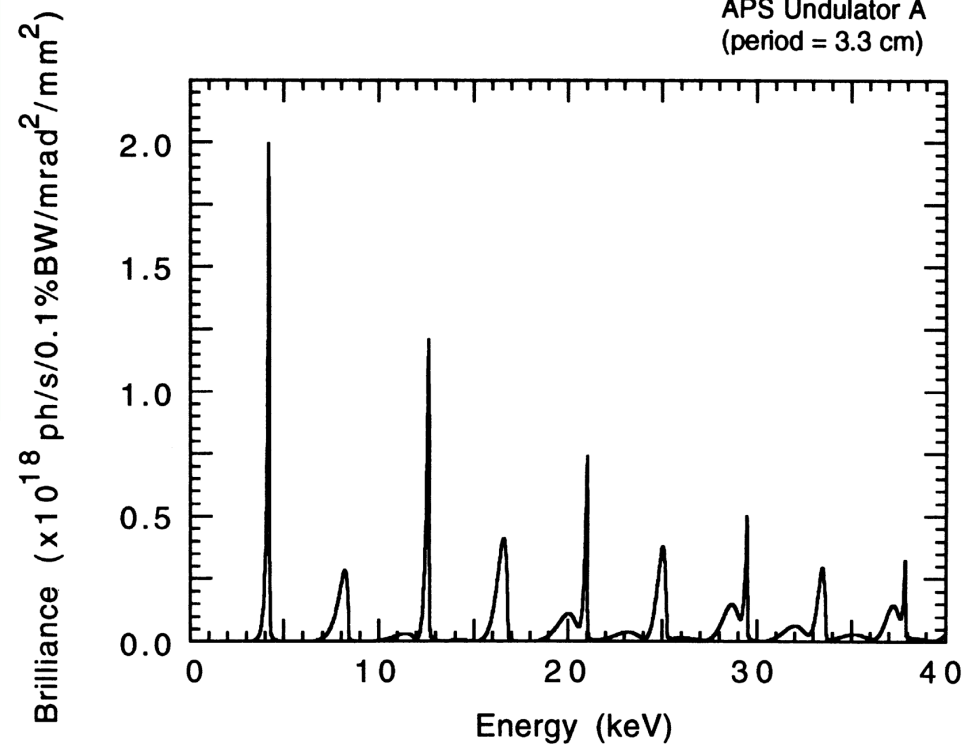
Diamond  
in-vacuum  
X-ray  
Undulator



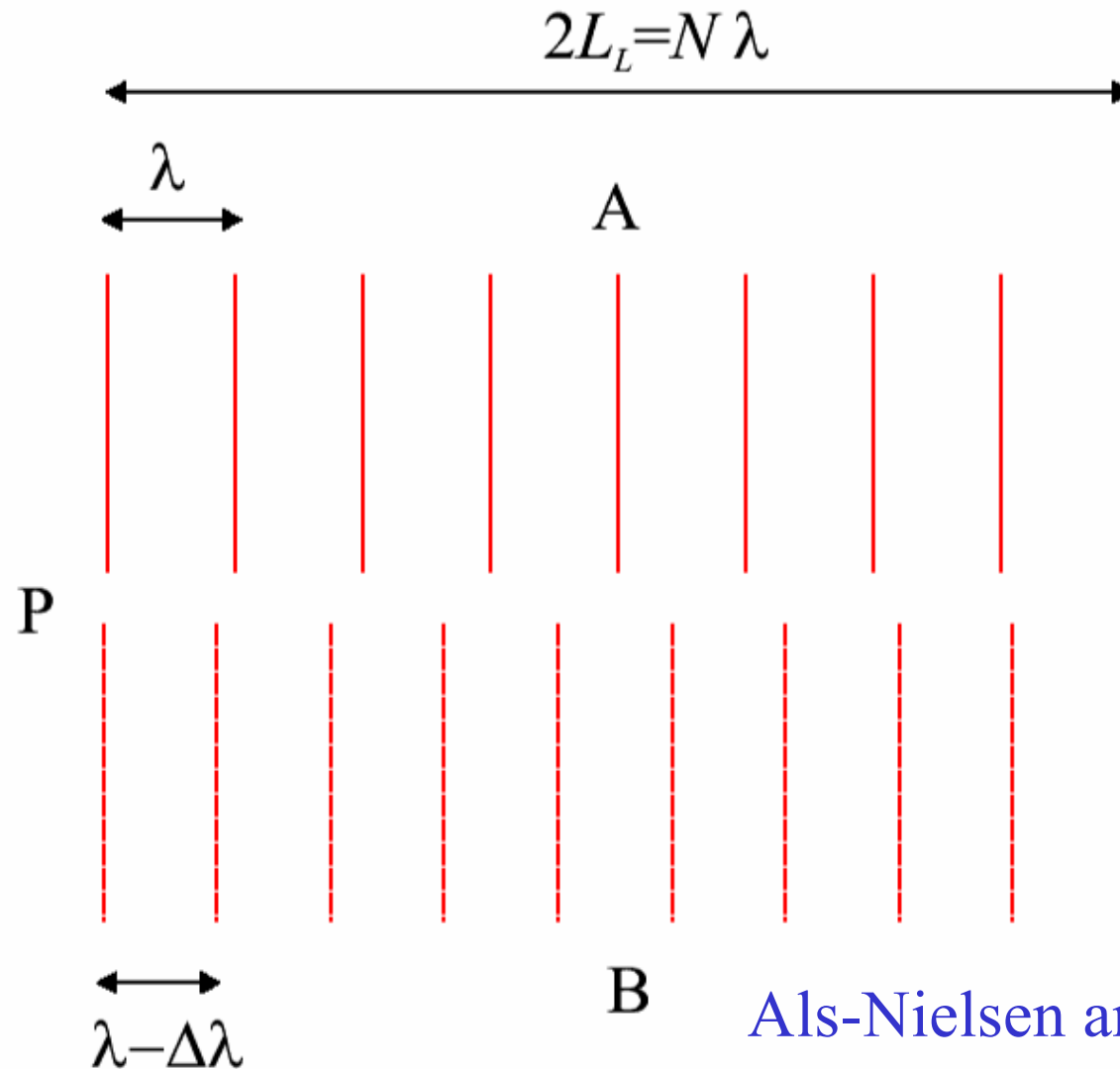
# X-ray Undulator Principle



$$\lambda_X = \frac{\lambda_U}{2\gamma^2} \left\{ 1 + \frac{K^2}{2} + (\gamma\theta)^2 \right\}$$



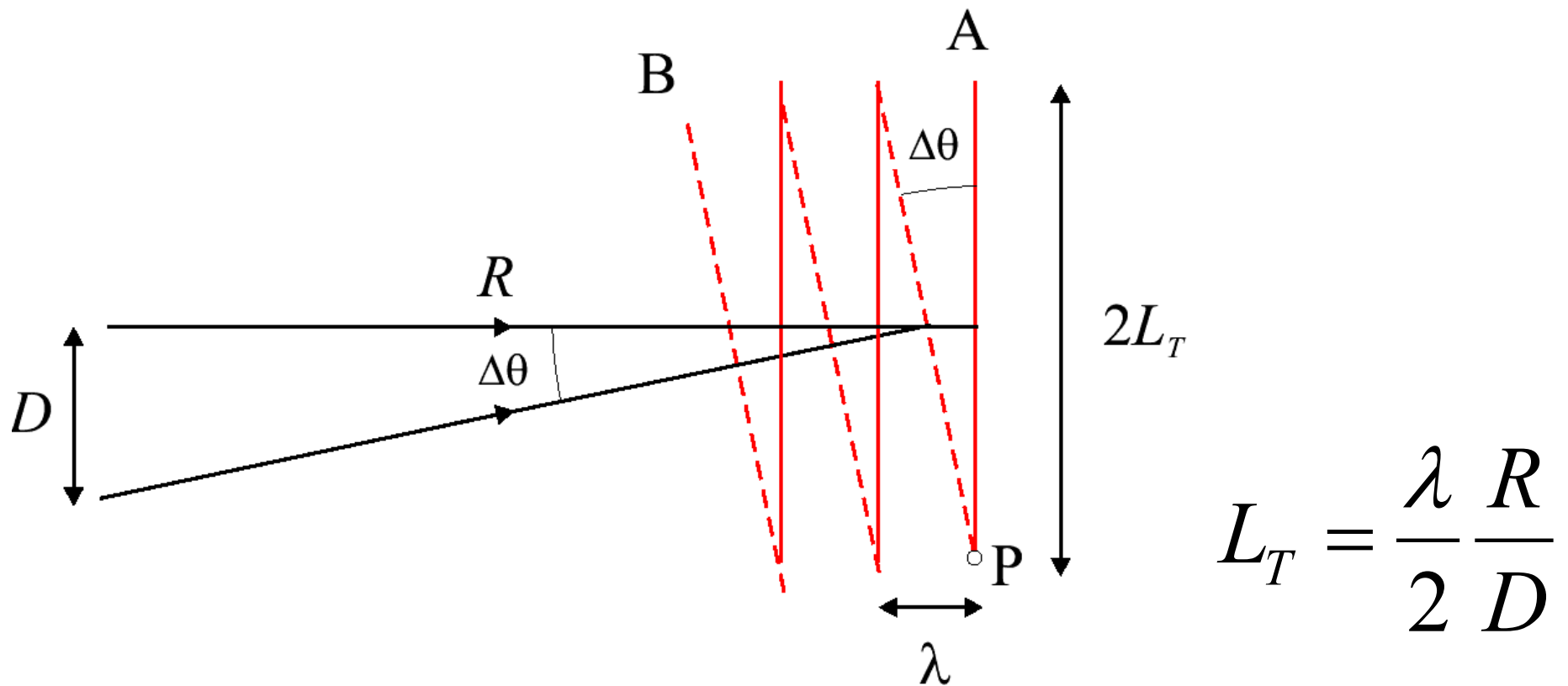
# Longitudinal Coherence



$$L_L = \frac{1}{2} \frac{\lambda^2}{\Delta\lambda}$$

Als-Nielsen and McMorro (2001)

# Lateral (Transverse) Coherence



$$L_T = \frac{\lambda R}{2 D}$$

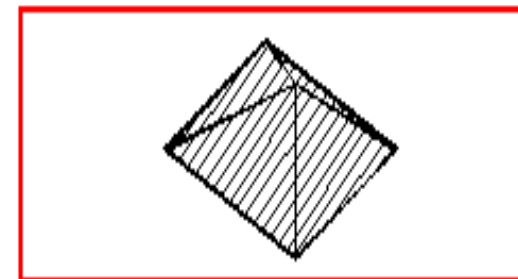
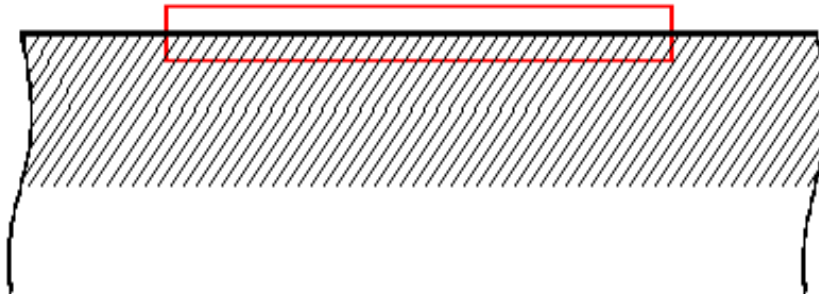
Als-Nielsen and McMorrow (2001)

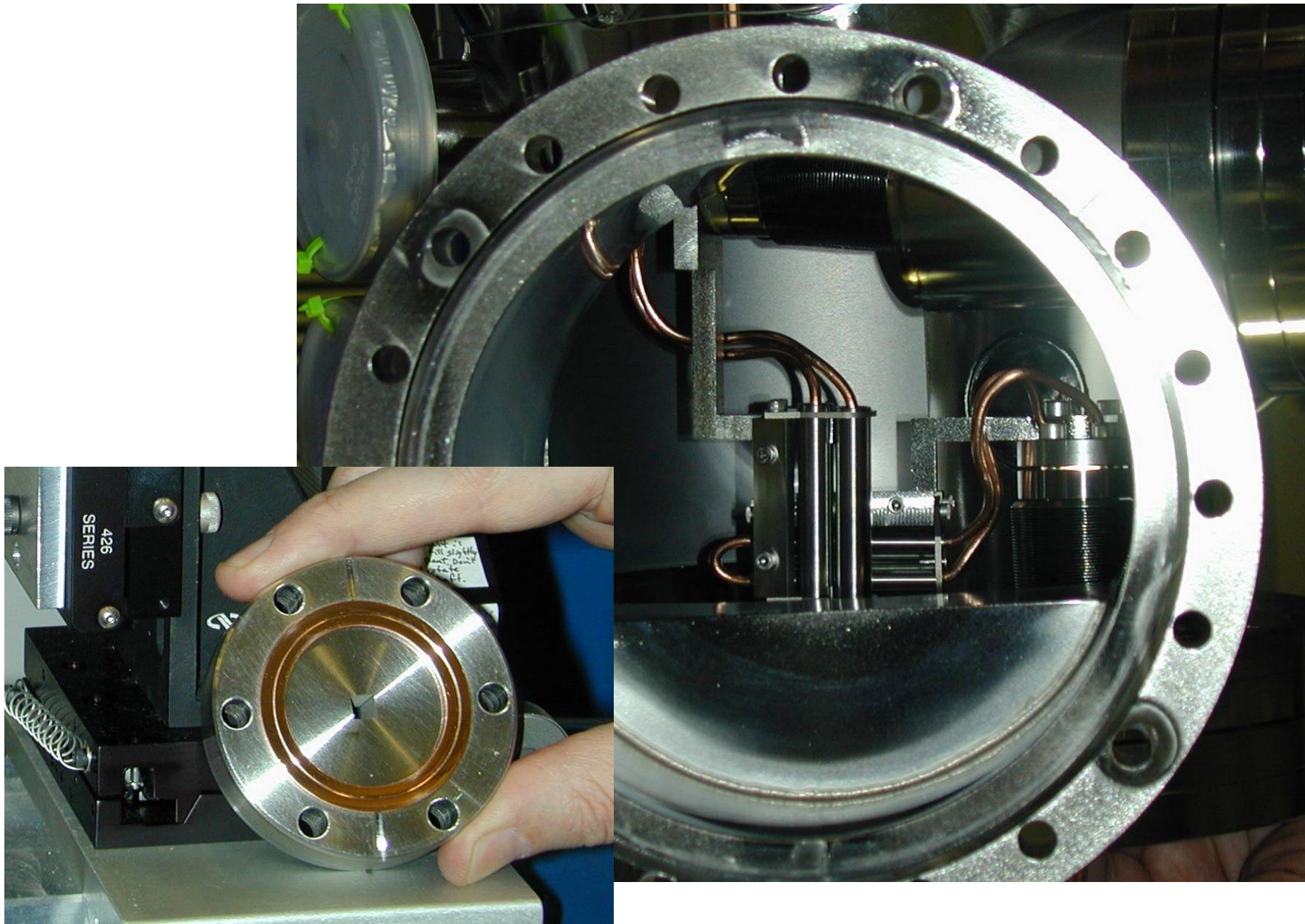
# Coherence at APS, ESRF or DLS

Typical of 3rd Generation (undulator) Synchrotron Source

Coherence of	$\xi_{\text{VER}}$	$\xi_{\text{HORIZ}}$	$\xi_{\text{LONG}}$	Flux
Raw Undulator	35 $\mu\text{m}$	9 $\mu\text{m}$	0.004 $\mu\text{m}$	$2 \times 10^{12}$
Si(111) Monochromator	35 $\mu\text{m}$	9 $\mu\text{m}$	1 $\mu\text{m}$	$1 \times 10^{10}$
C(111) Monochromator	35 $\mu\text{m}$	9 $\mu\text{m}$	3 $\mu\text{m}$	$3 \times 10^9$

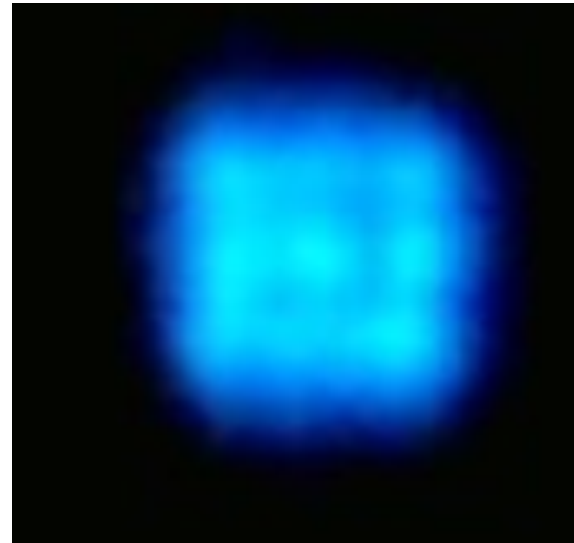
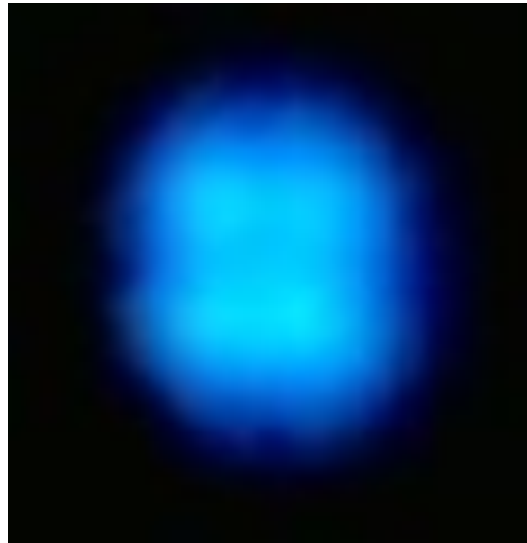
Coherent region defined by slits



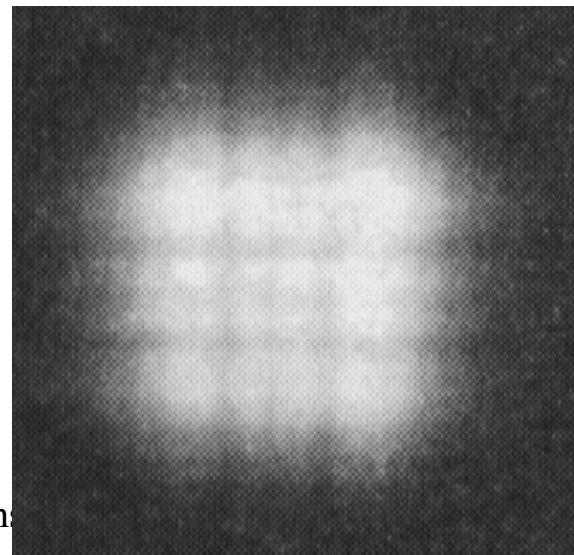
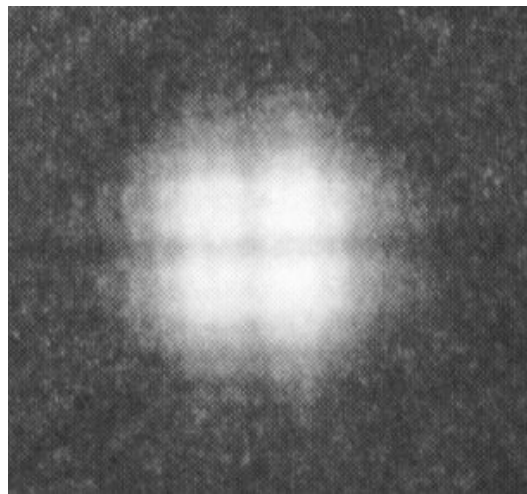


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# Fresnel Diffraction when $d^2 \sim \lambda D$



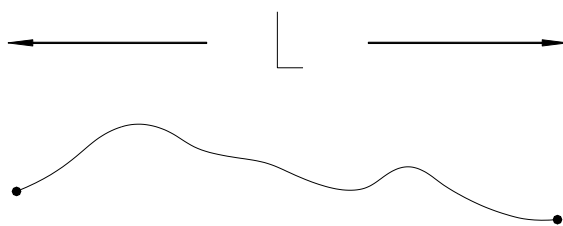
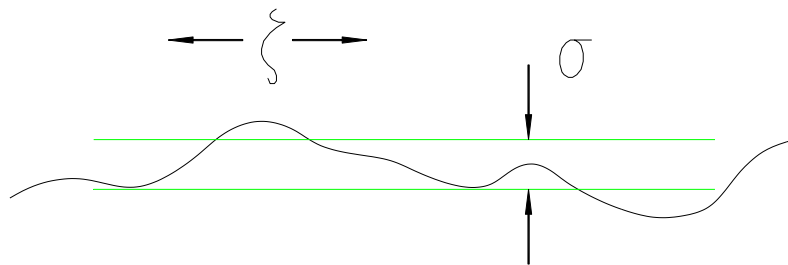
X-ray  
beam  
defined  
by RB  
slits



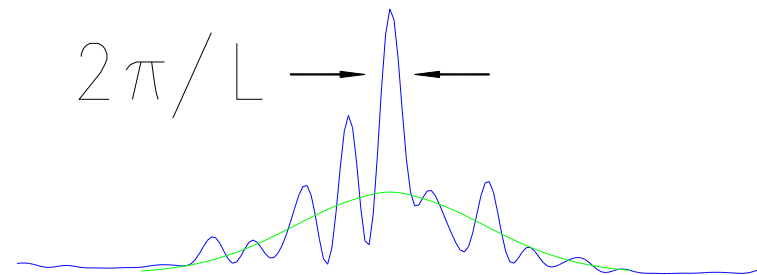
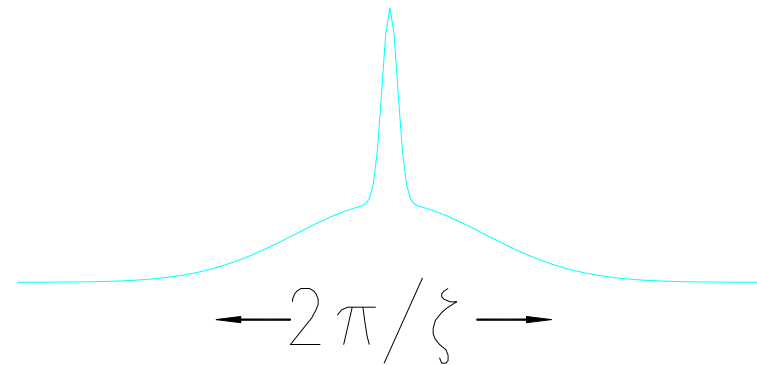
Visible  
Fresnel  
diffraction  
from  
Hecht  
“Optics”

# Diffuse Scattering acquires Structure using CXD

Real Space

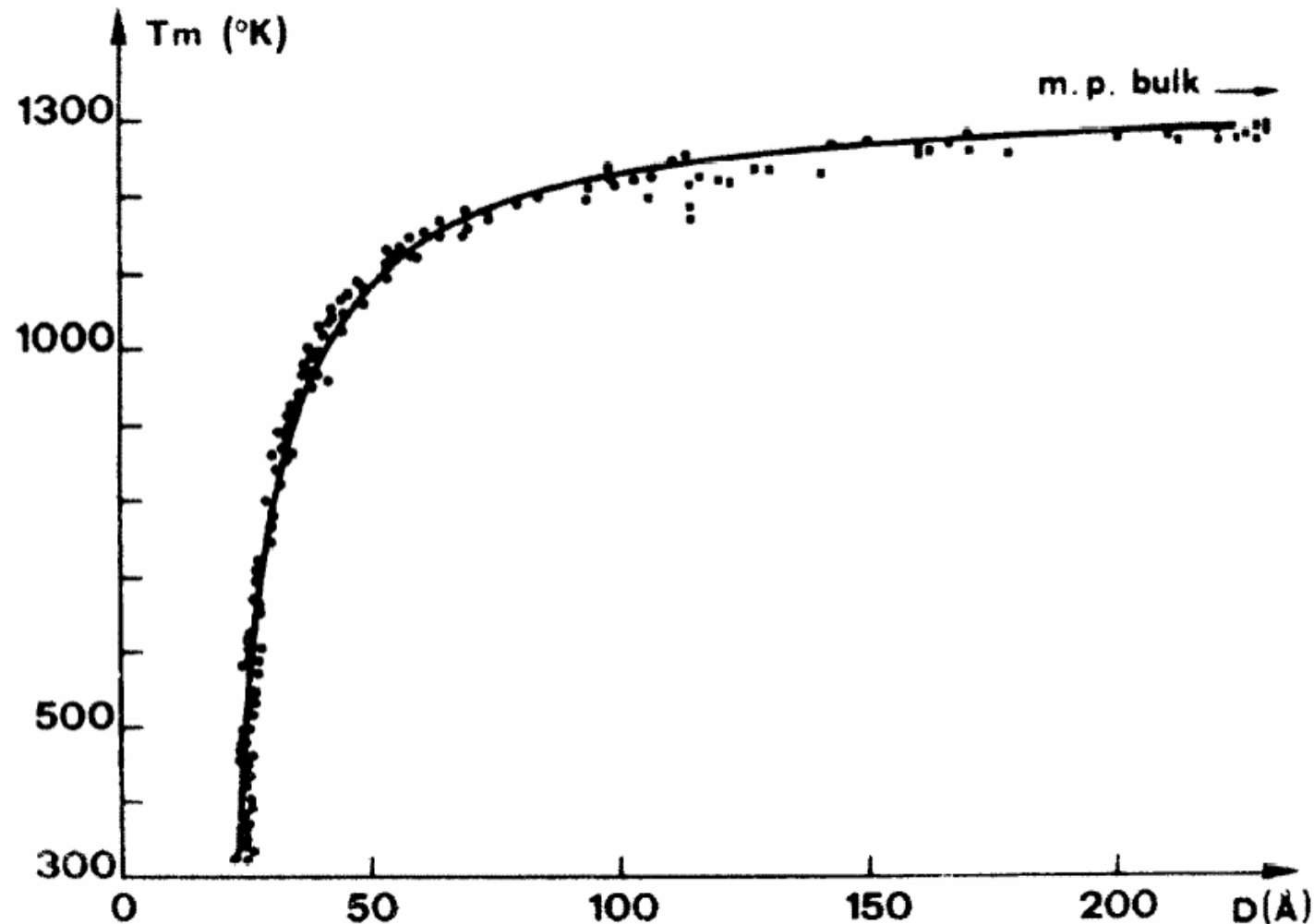


Reciprocal Space

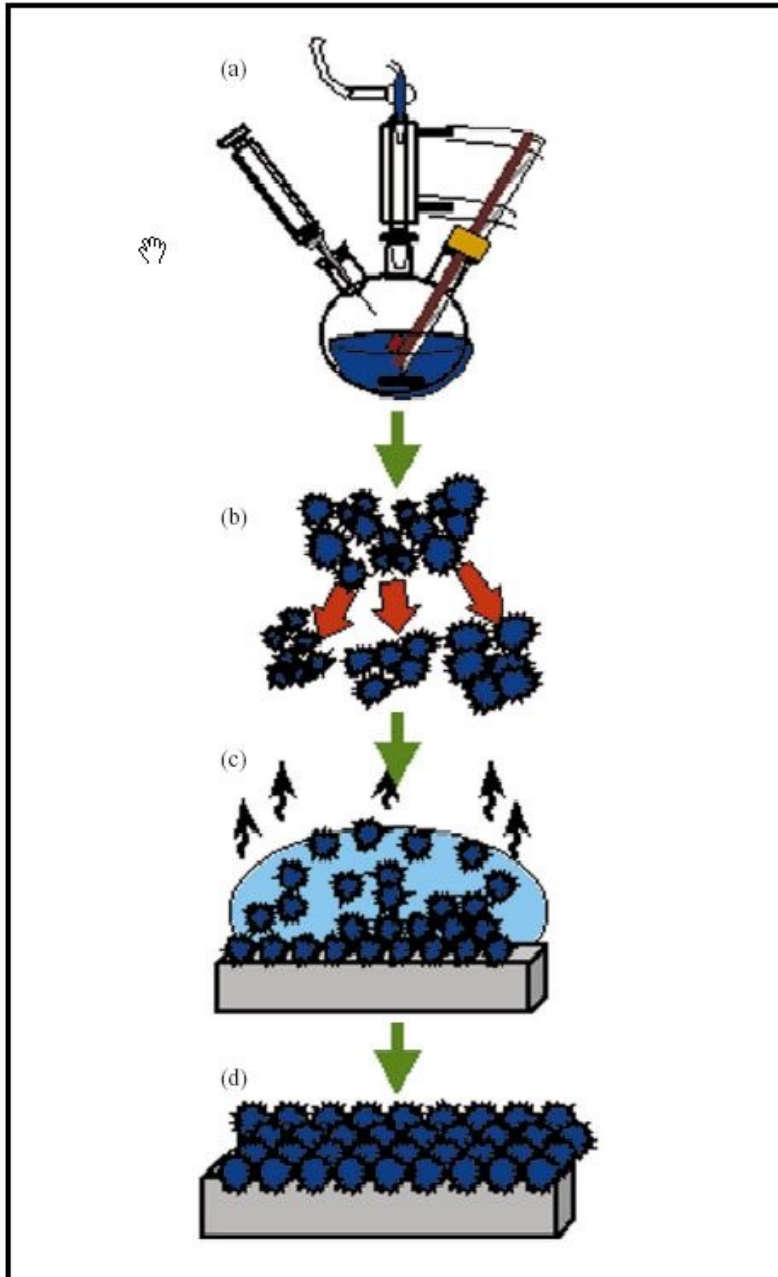


# Size-dependent Melting of Au Particles

P. Buffat and J-P. Borel, Phys. Rev. A 2287-97 (1975)

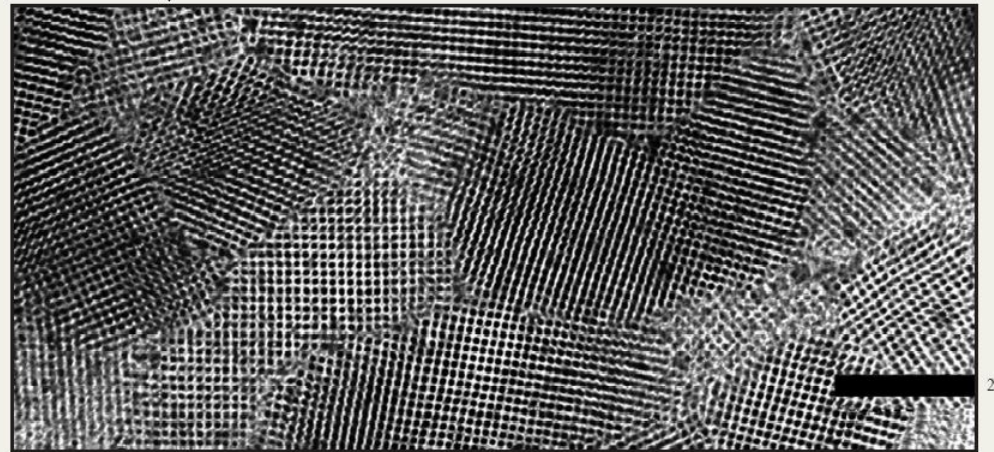


# Chemical Synthesis of Nanocrystals

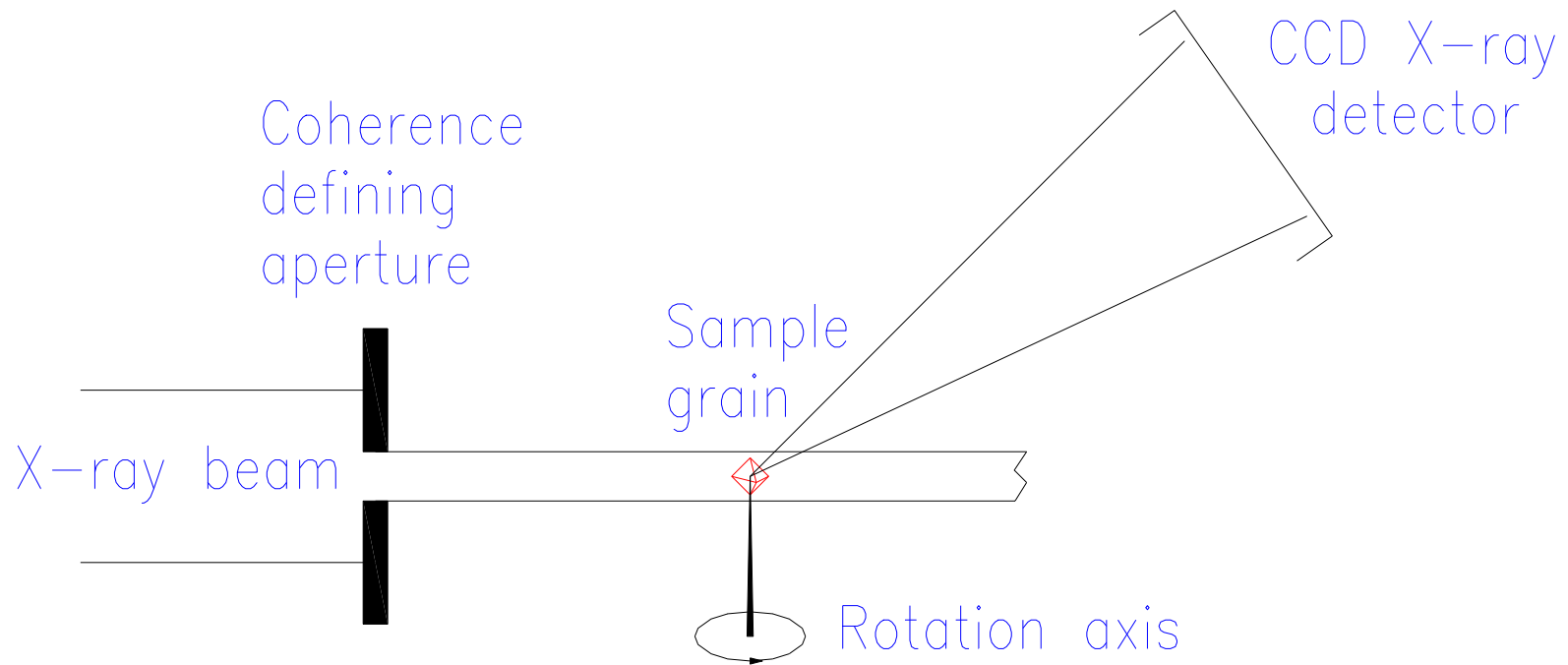


- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

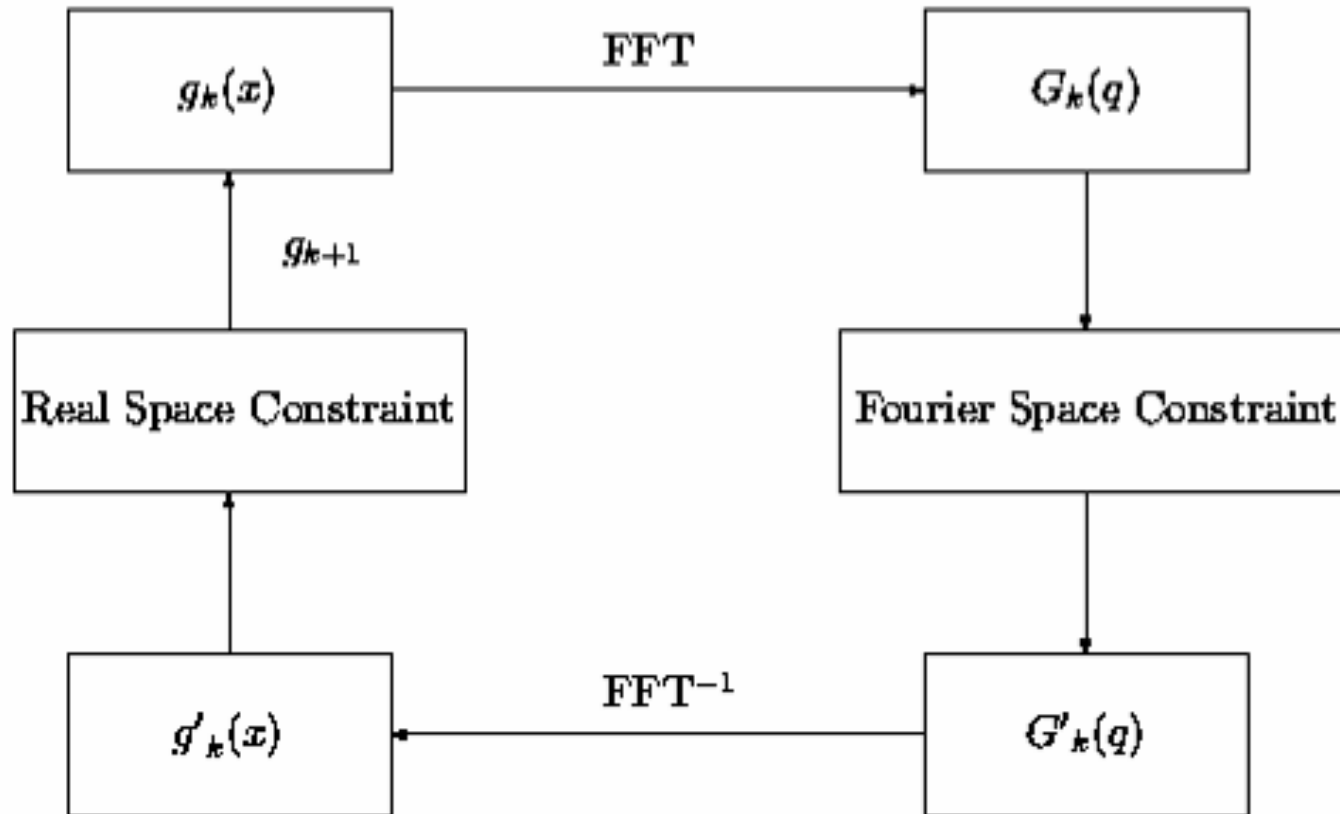
C. B. Murray, IBM J. Res. & Dev. **45**  
**47** (2001)



# Lensless X-ray Microscope



# Generic “Error Reduction” method



J. R. Fienup *Appl. Opt.* 21 2758 (1982)

R. W. Gerchberg and W. O. Saxton *Optik* 35 237 (1972)

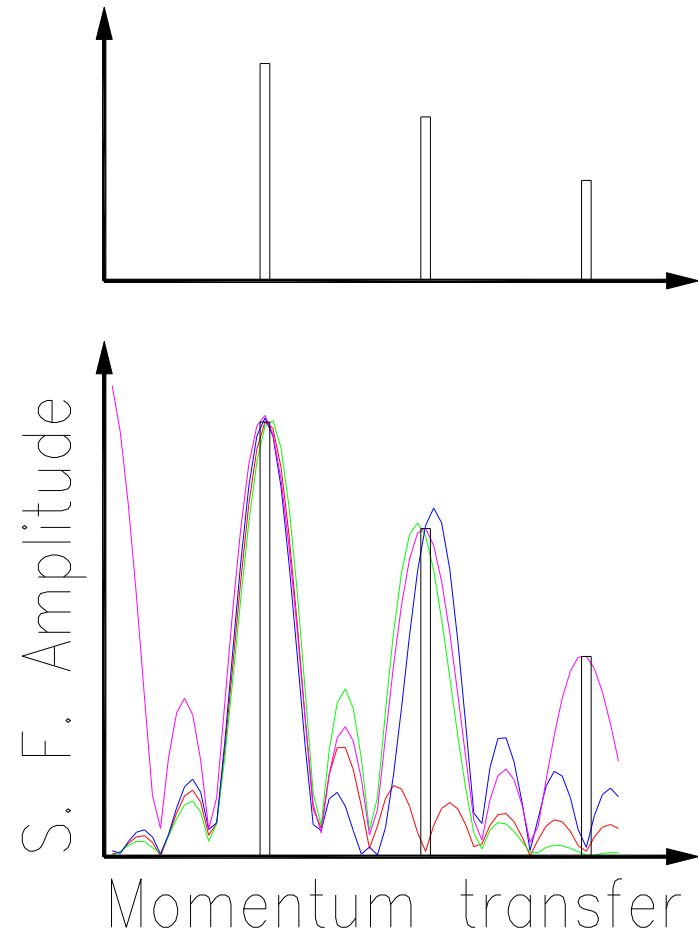
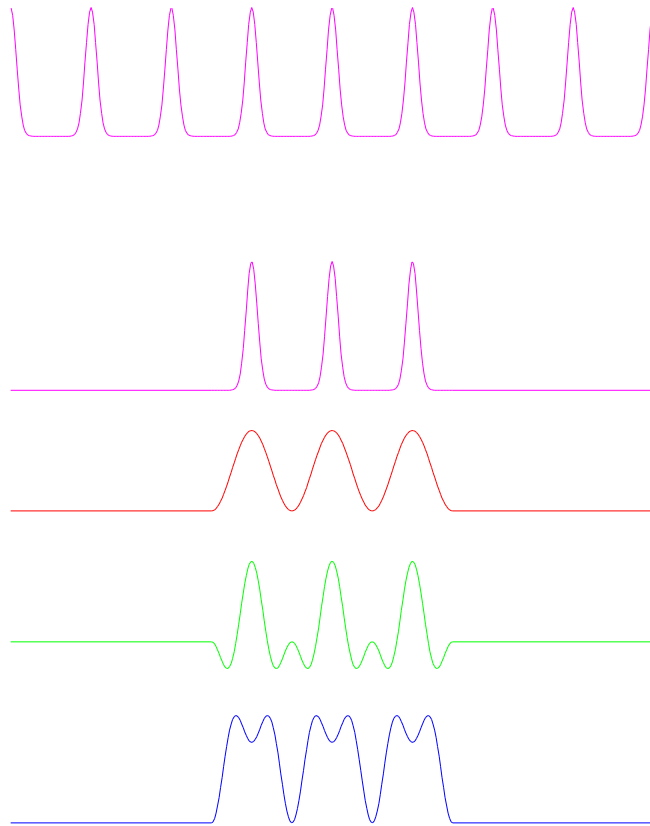
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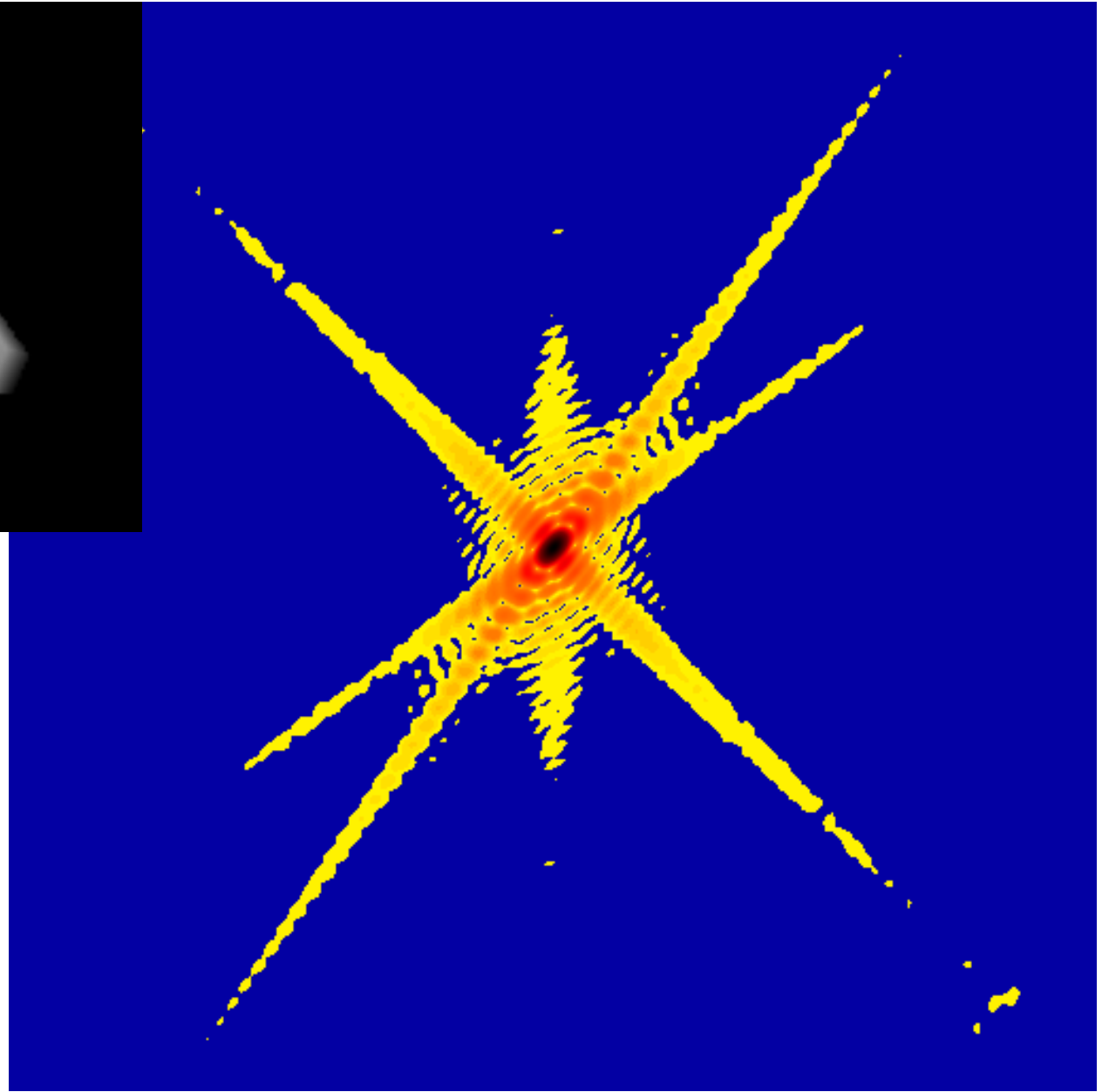
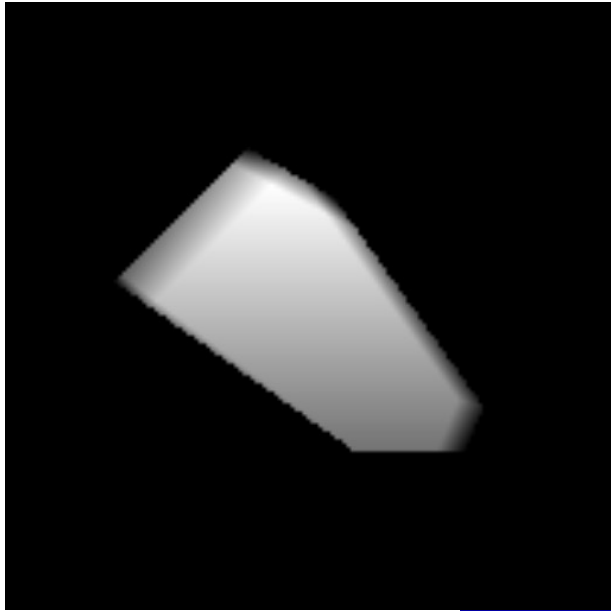
# Real-space Constraints in Crystallography

R. P. Millane, J. Opt. Soc Am. A **13** 725 (1996)

- ‘Positivity’ and ‘Atomicity’ constraints (Sayre)
- Finite **support**, molecular envelope
- Solvent flattening/Molecular replacement
- Non-crystallographic symmetry
- Non-uniqueness is ‘pathologically rare’ ( $d > 1$ )
- Uses memory to avoid stagnation (Fienup HIO)

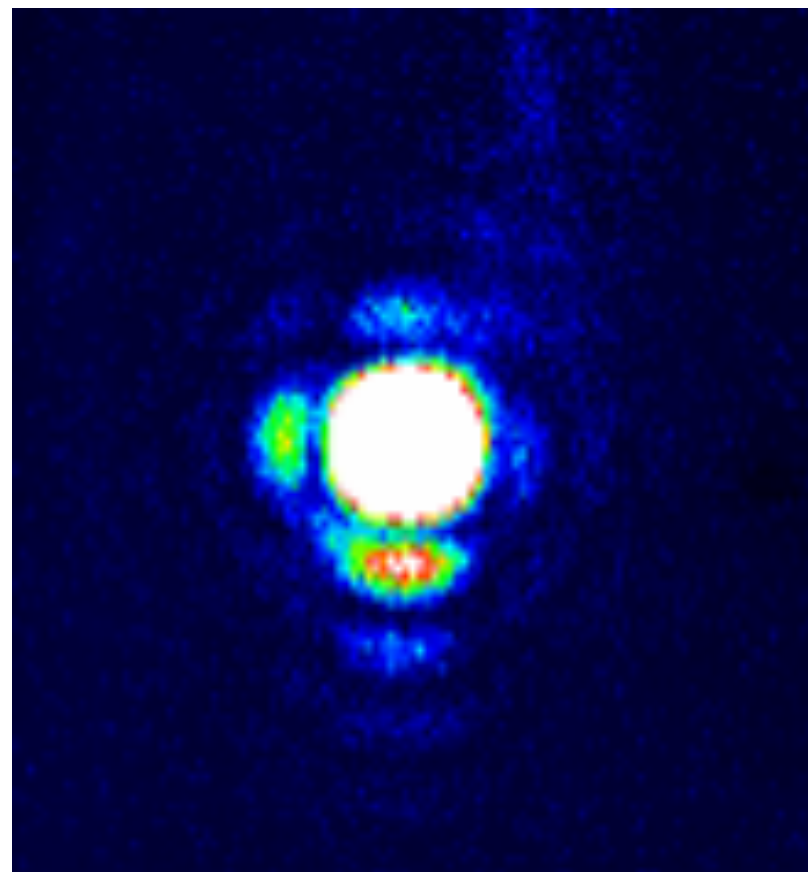
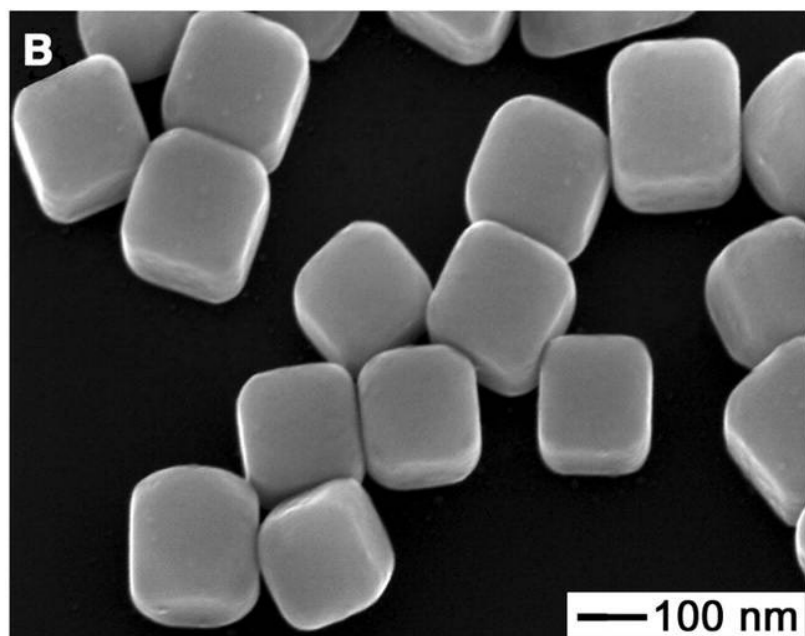
# Oversampling solves Phase Problem





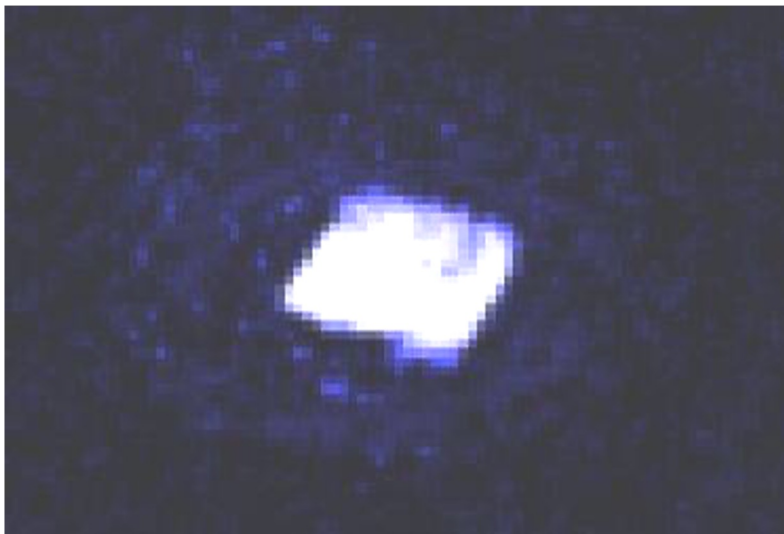
I. K. Robinson iNANO School

# Chemically Synthesized Silver Nanocubes

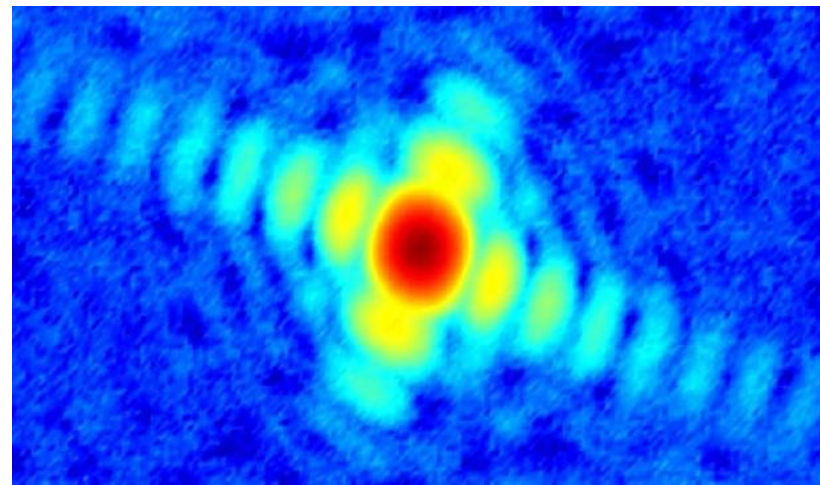
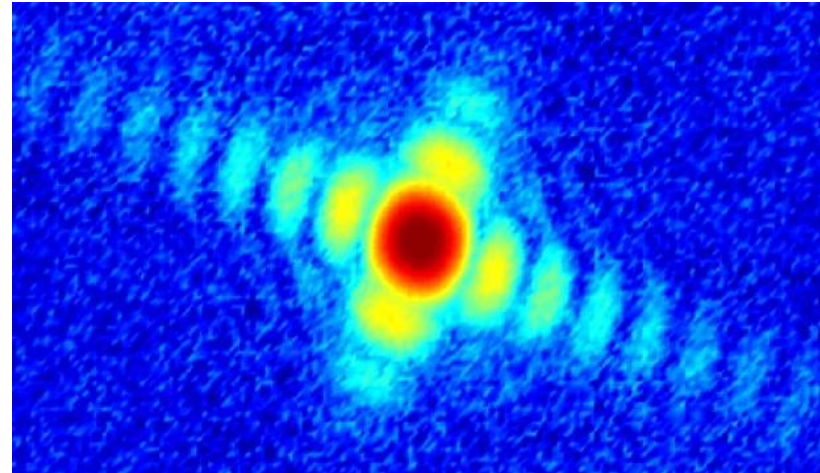


Yugang Sun and Younan Xia,  
*Science* 298 2177 (2003)

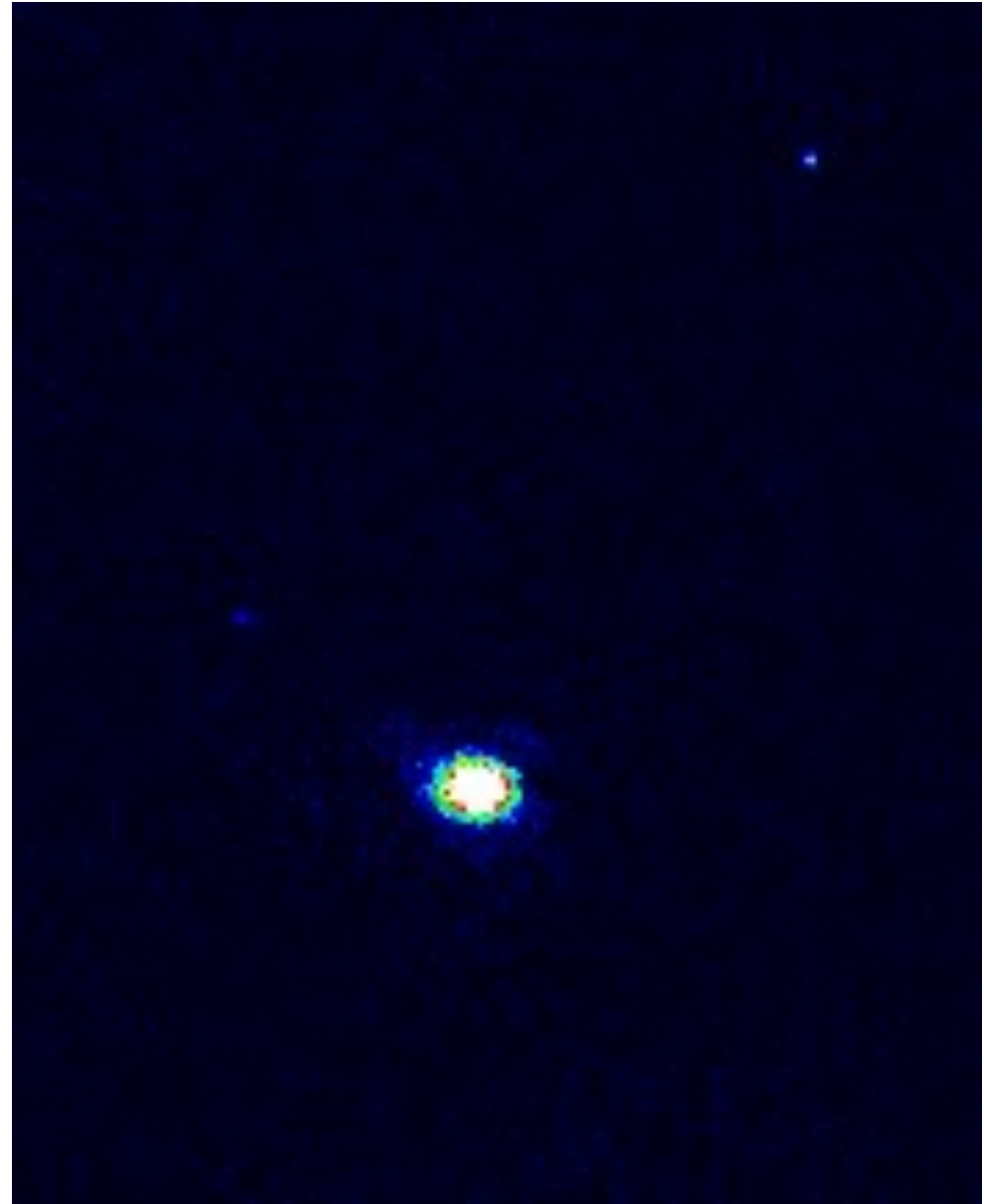
# Reconstruction of Ag Nanocrystal

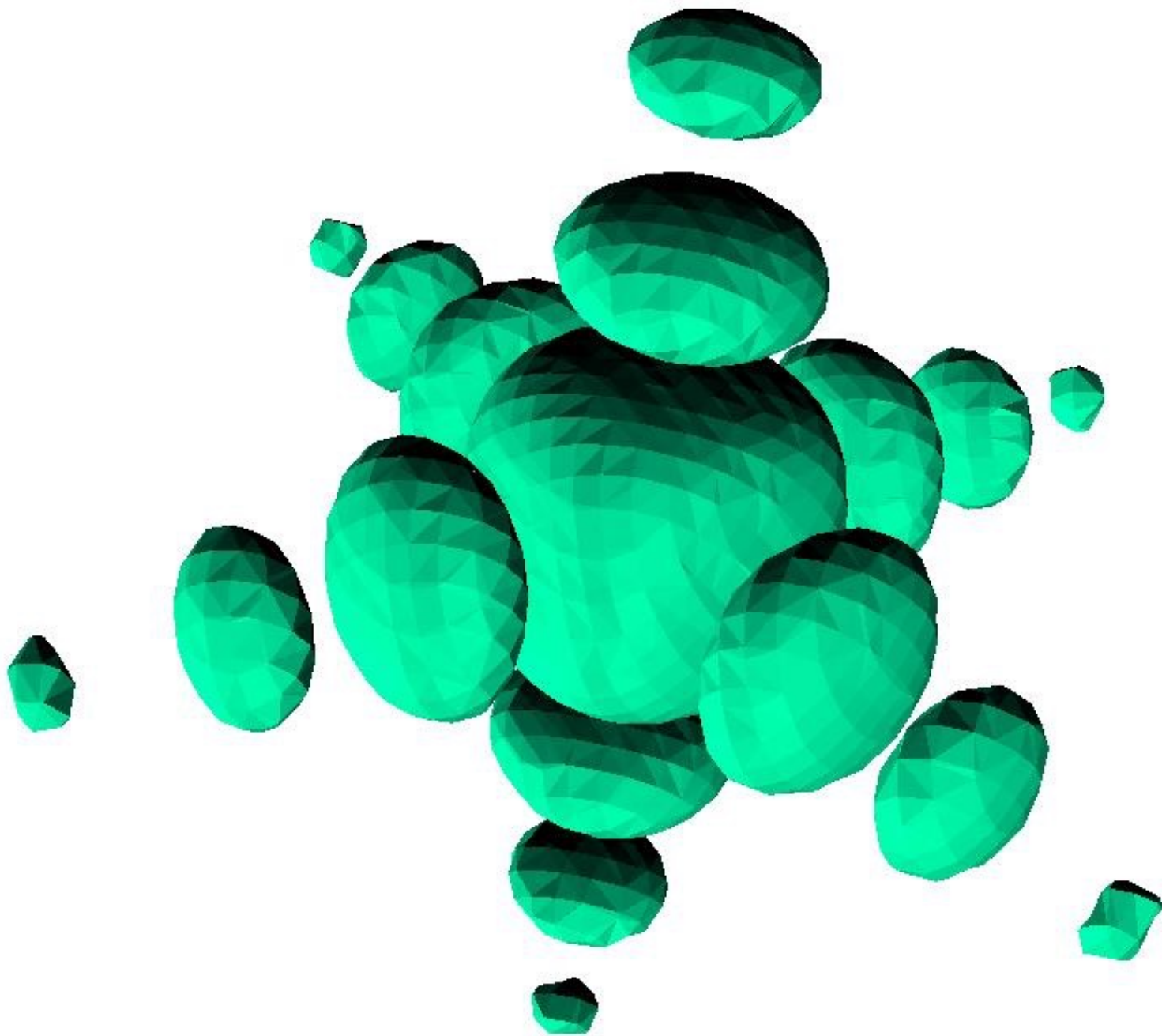


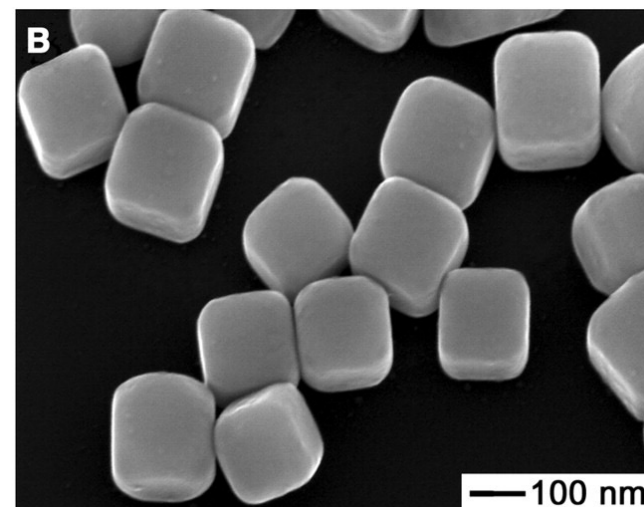
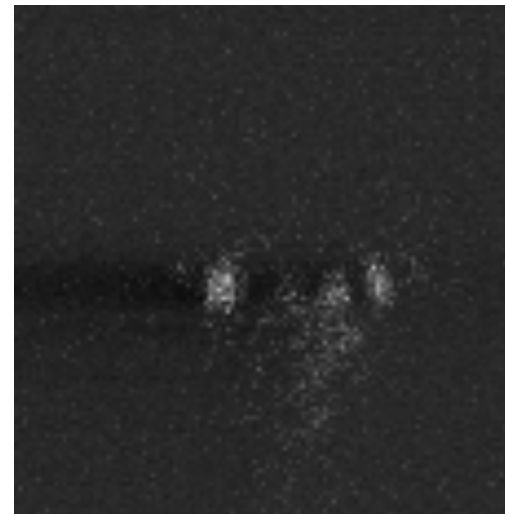
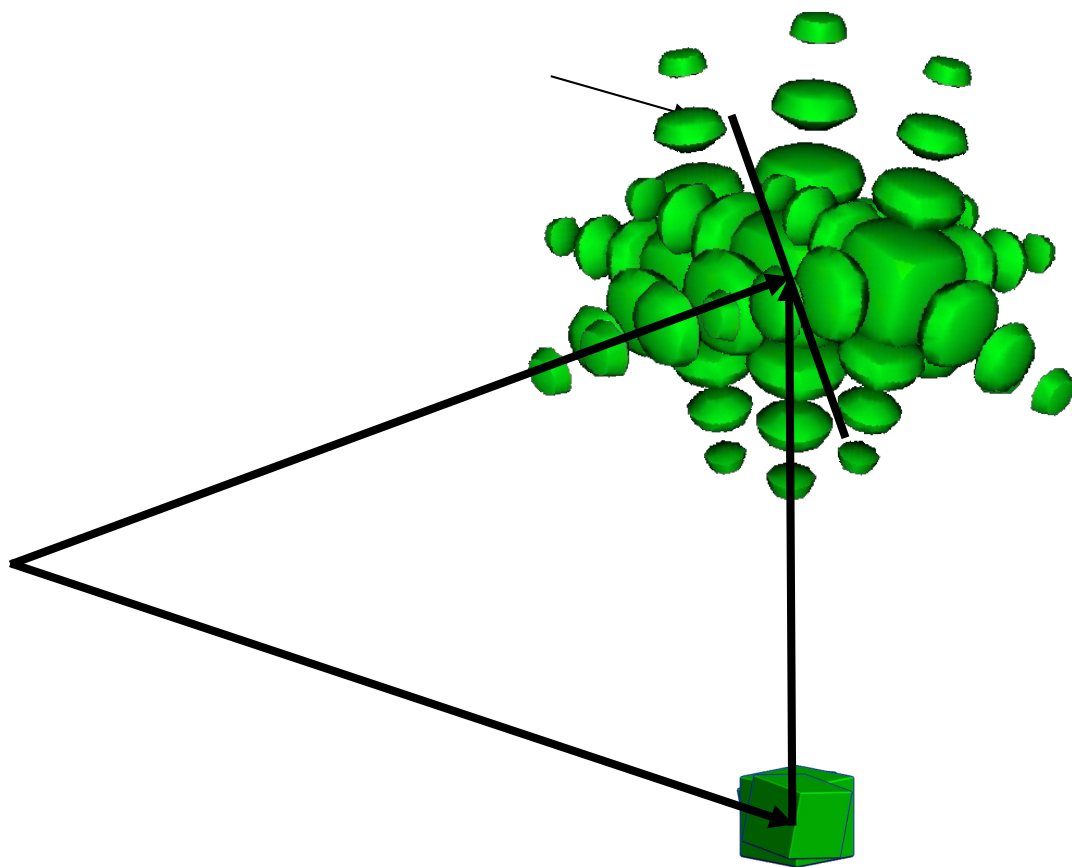
←→  
200nm

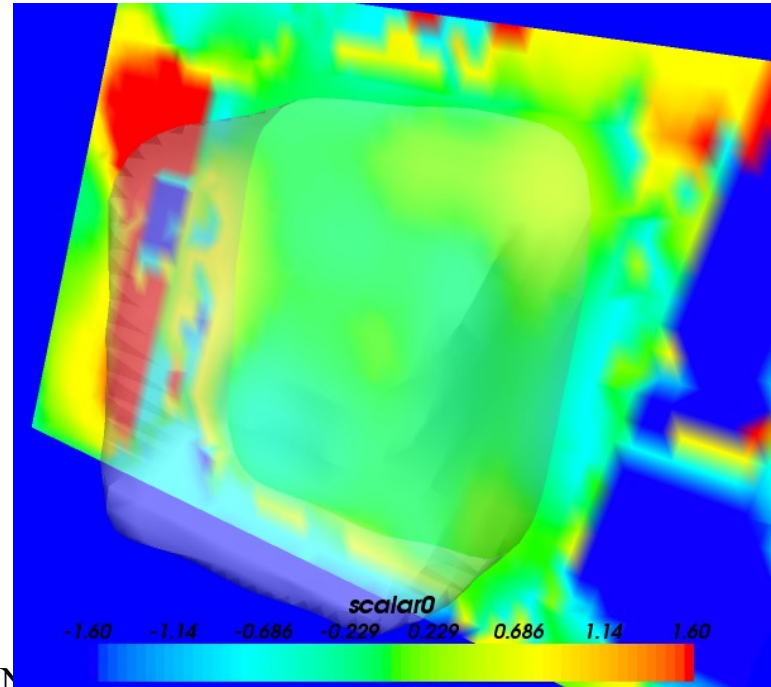
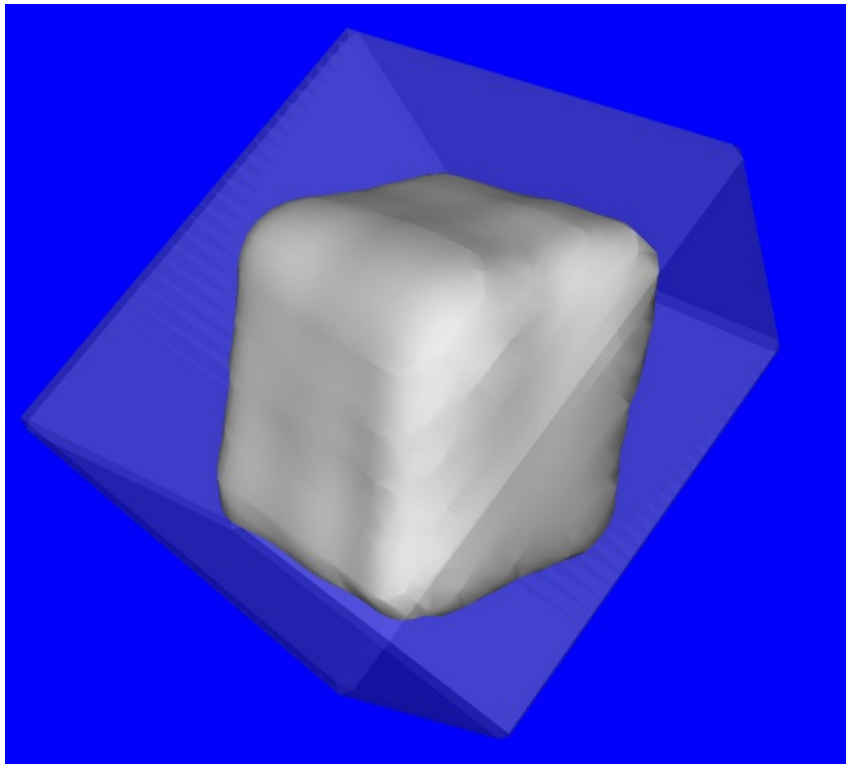
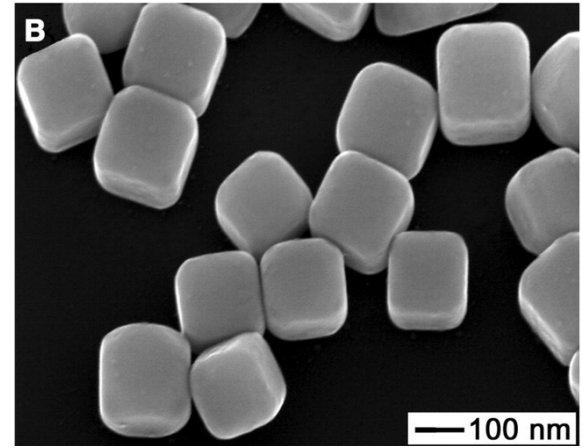
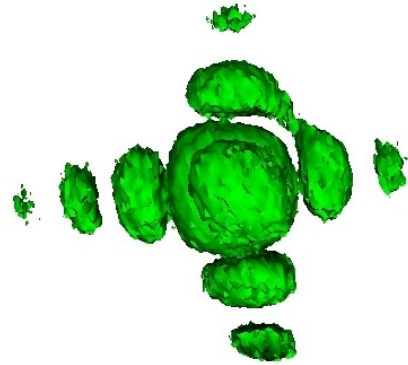
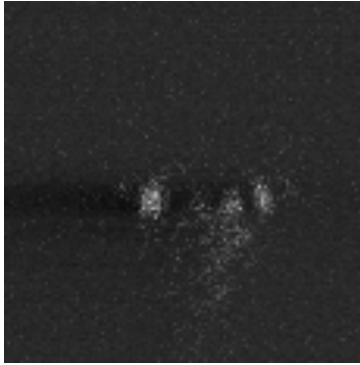


Rocking  
scan of Ag  
cubes with  
 $0.01^\circ$  steps

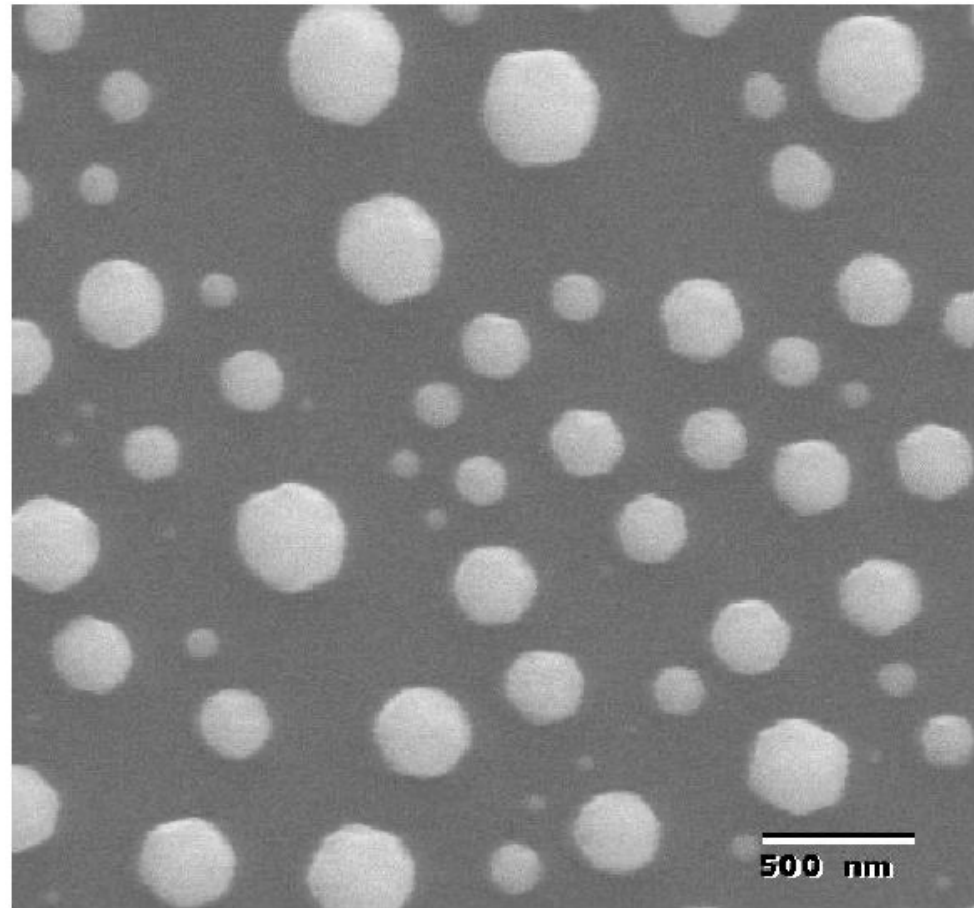




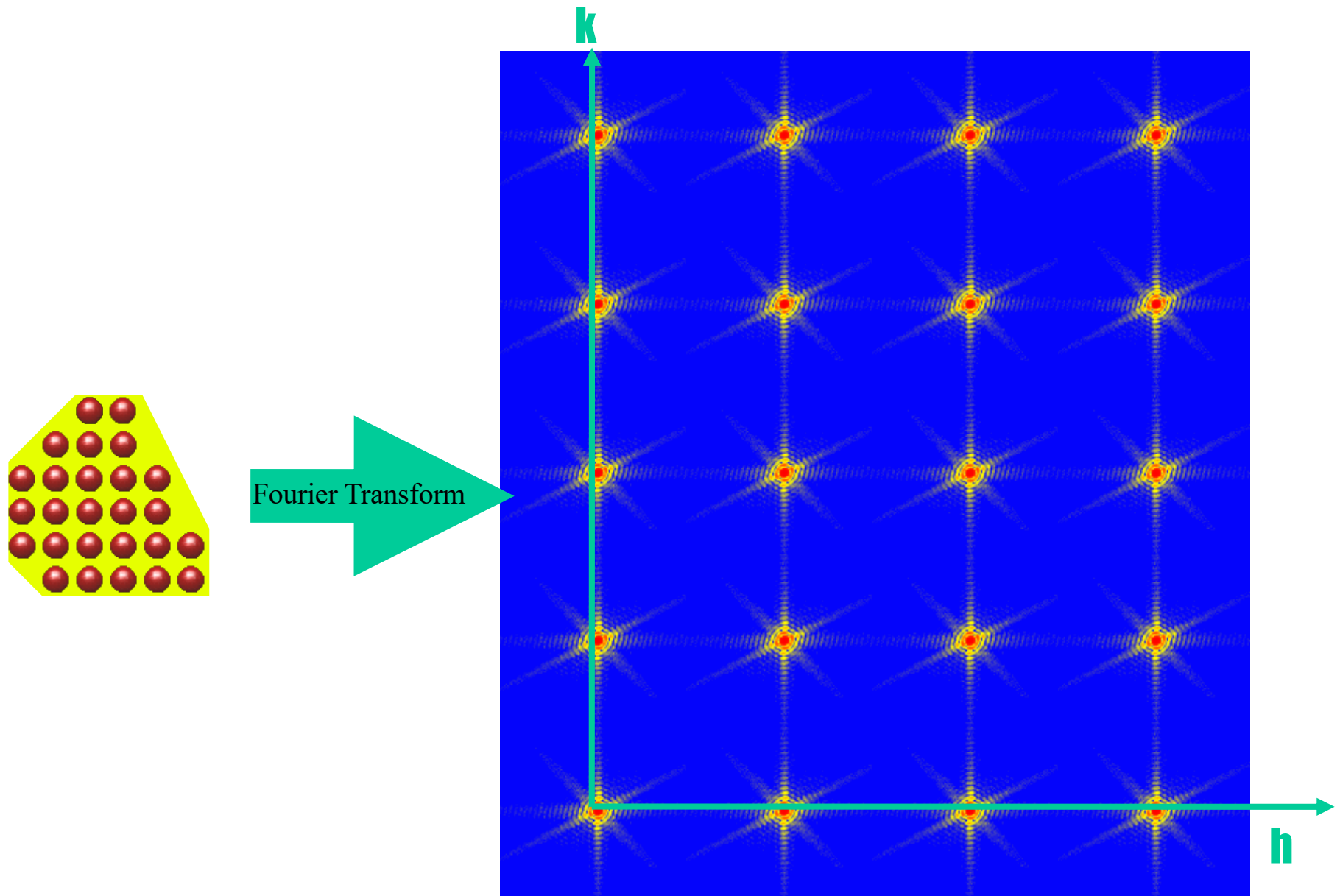




# In situ growth of Pb crystals



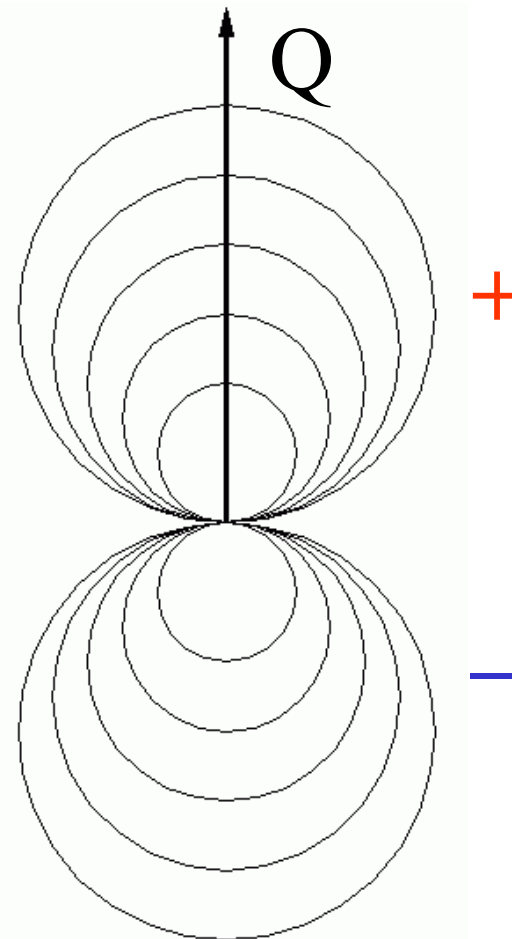
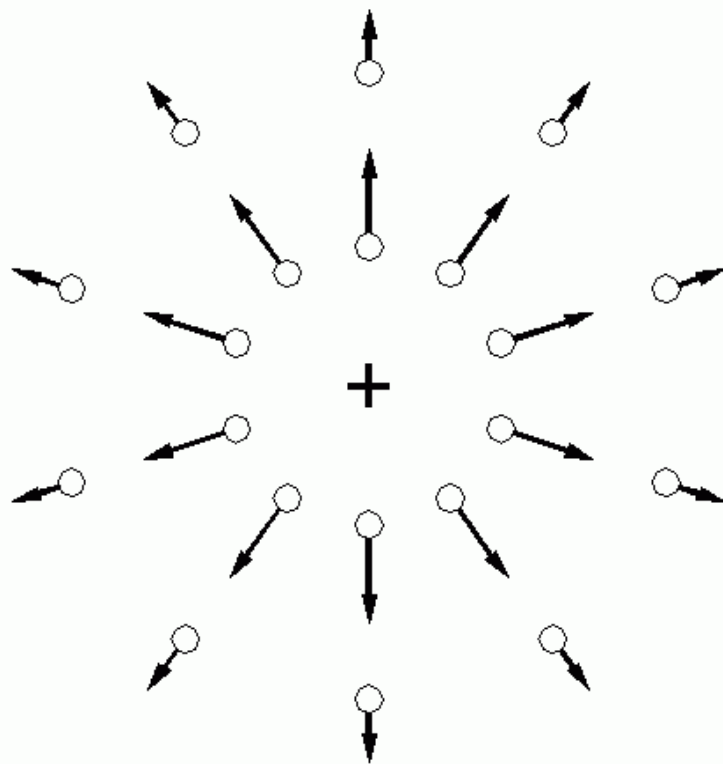
# Coherent Diffraction from Crystals



# Diffraction by Strain of Point Defect

$$A \sim \sum e^{i\mathbf{Q}\cdot(\mathbf{R}_j+\mathbf{u}_j)}$$
$$\approx \sum e^{i\mathbf{Q}\cdot\mathbf{R}_j} (1+i\mathbf{Q}\cdot\mathbf{u}_j)$$

Imaginary density



# Good statistics, 3D diffraction data

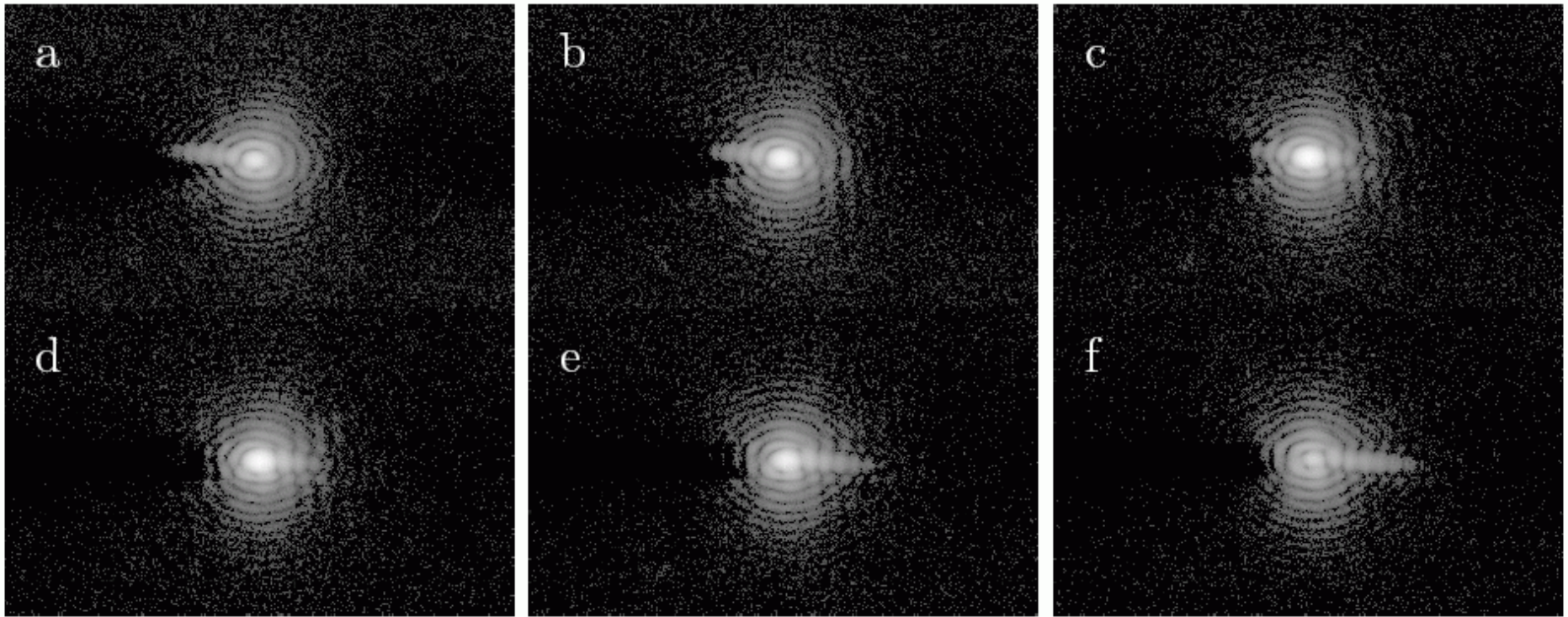
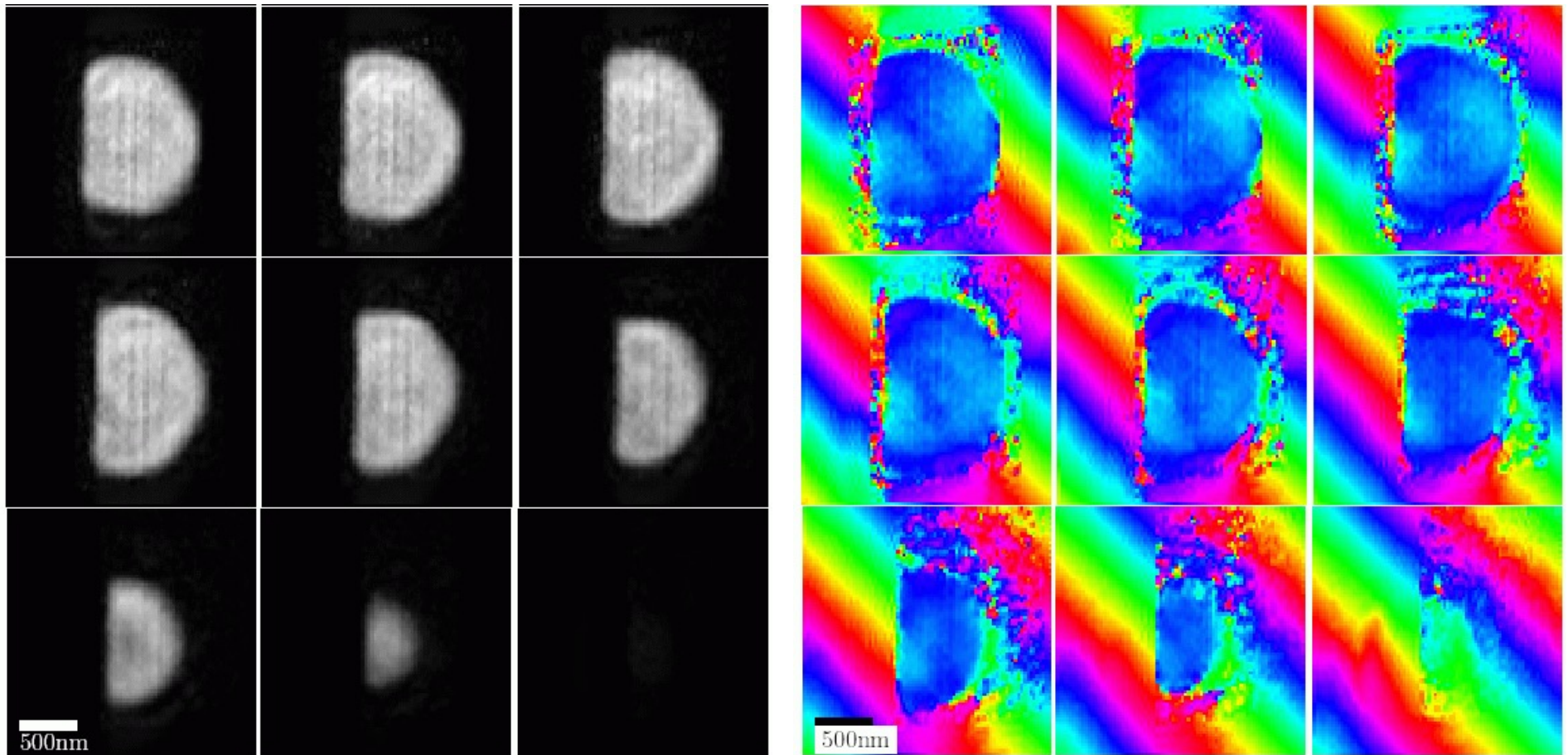
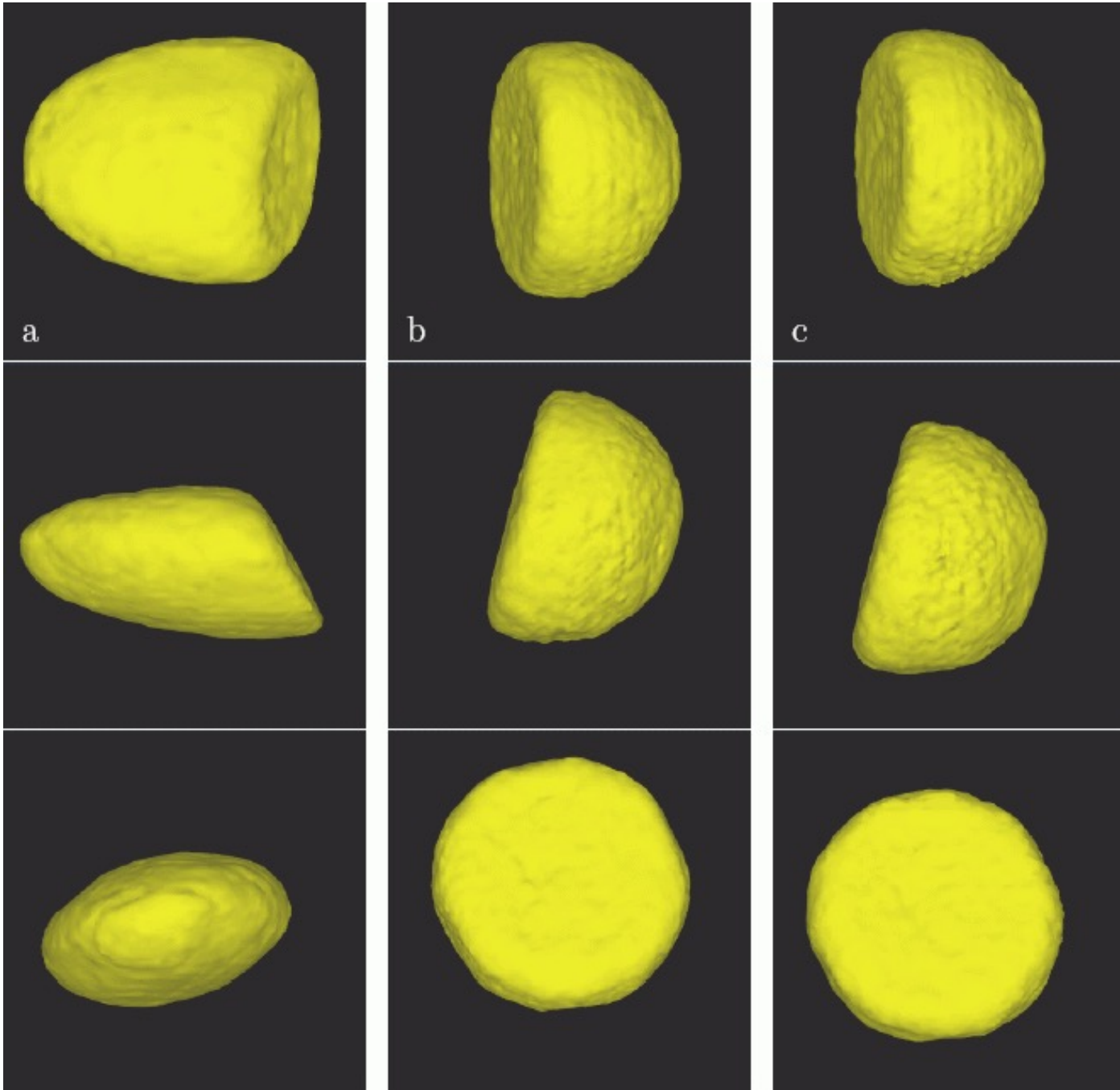


Figure 4.12: Center slices from 3D CXD pattern from Pb sample, on a log scale. Data file 296 from 10/03.

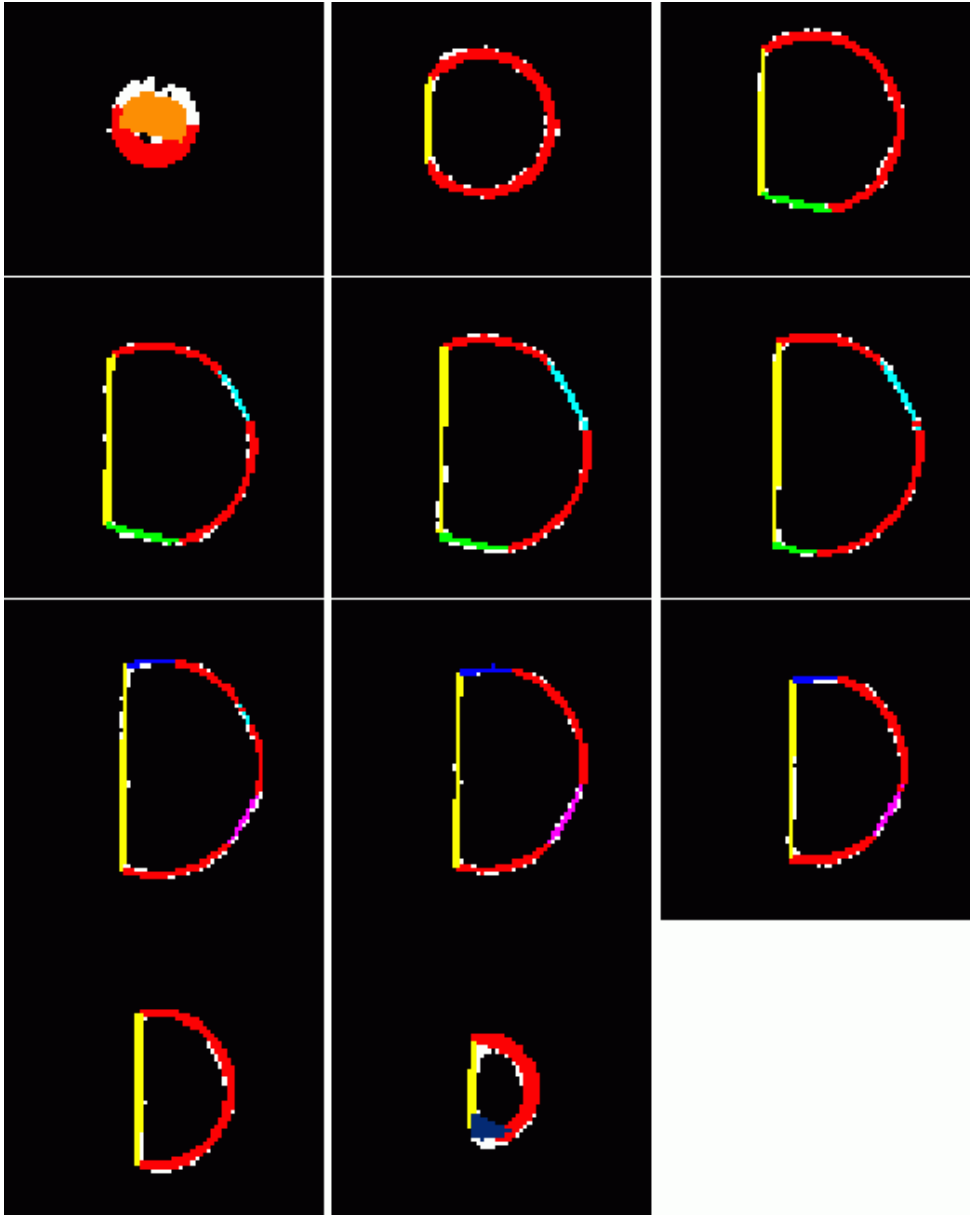
# Complex Density (amplitude *and* phase)












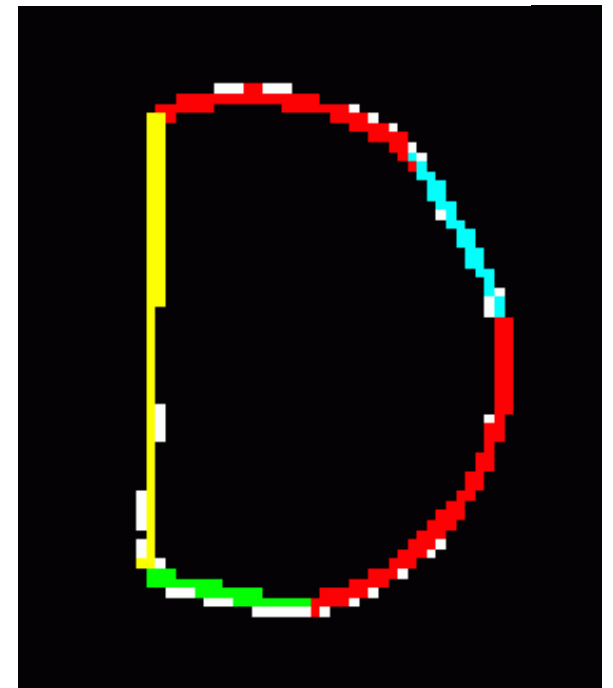
I. K. Robinson iNANO School

# Fitting to faceted shape

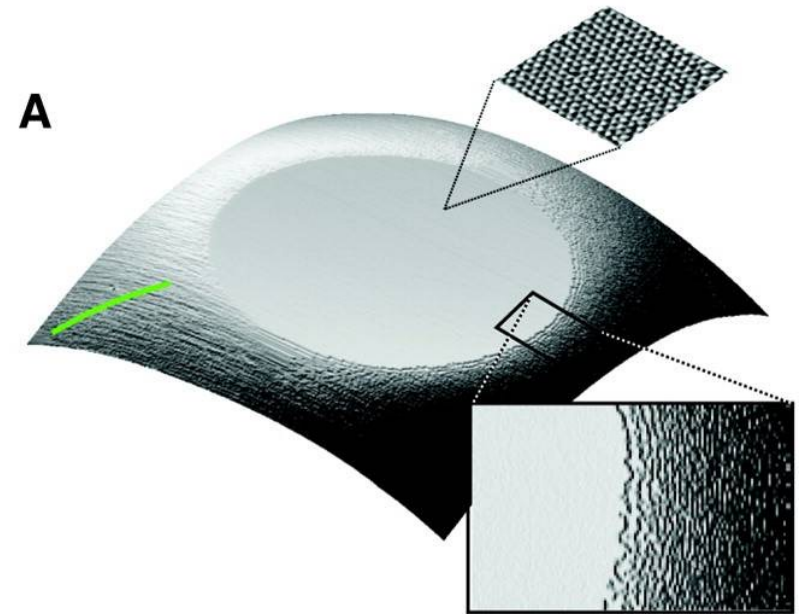


	$ R $		P0	P1	P2	P3	P4	P5	P6
	9.4	P0	0	85	149	79	134	106	71
	25.7	P1		0	123	164	83	76	102
	25.1	P2			0	72	67	74	110
	25.9	P3				0	111	106	76
	25.4	P4					0	113	68
	25.4	P5						0	176
	26.0	P6							0 0

Angles between facets

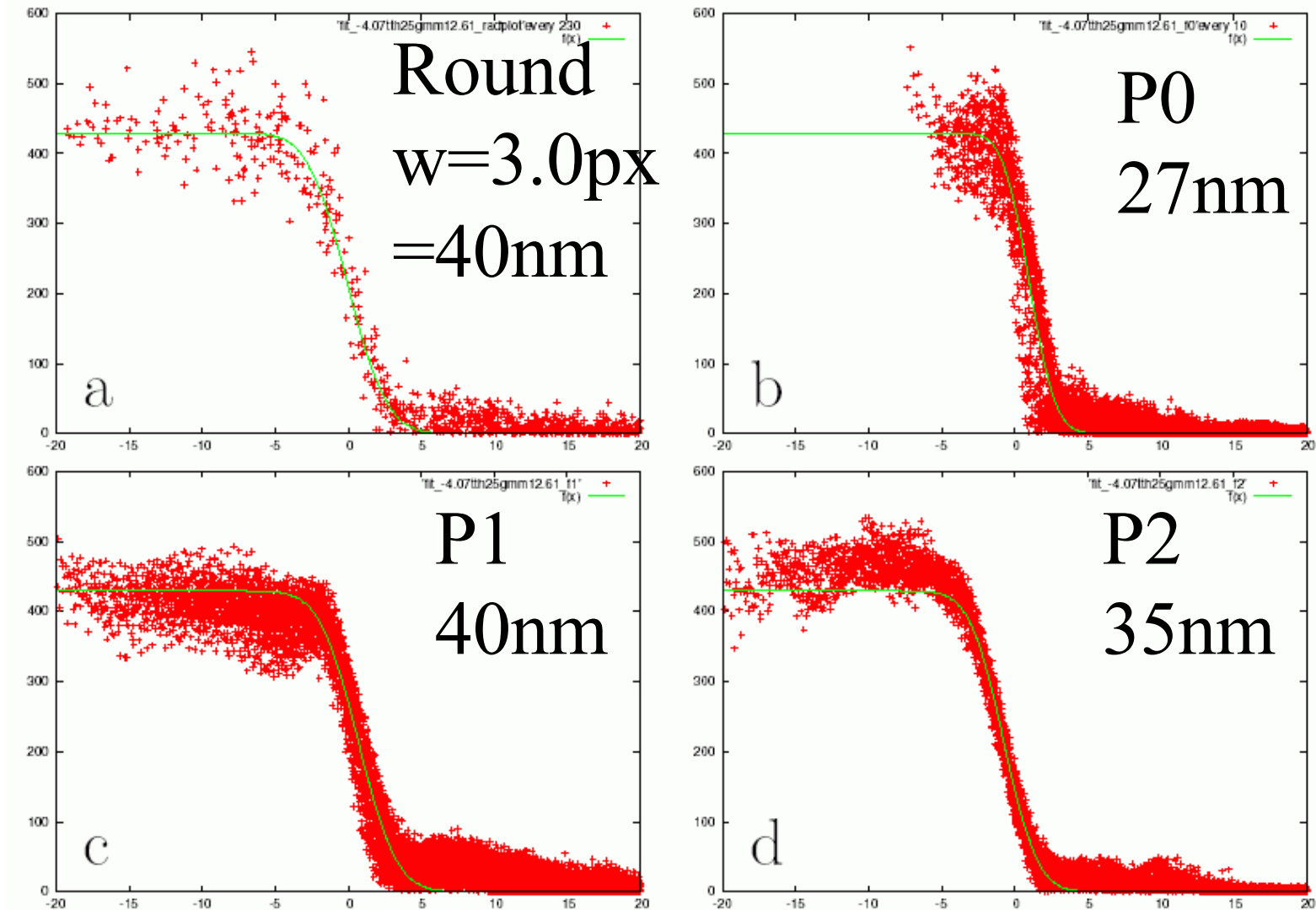


# Facets of Equilibrium Crystal Shape

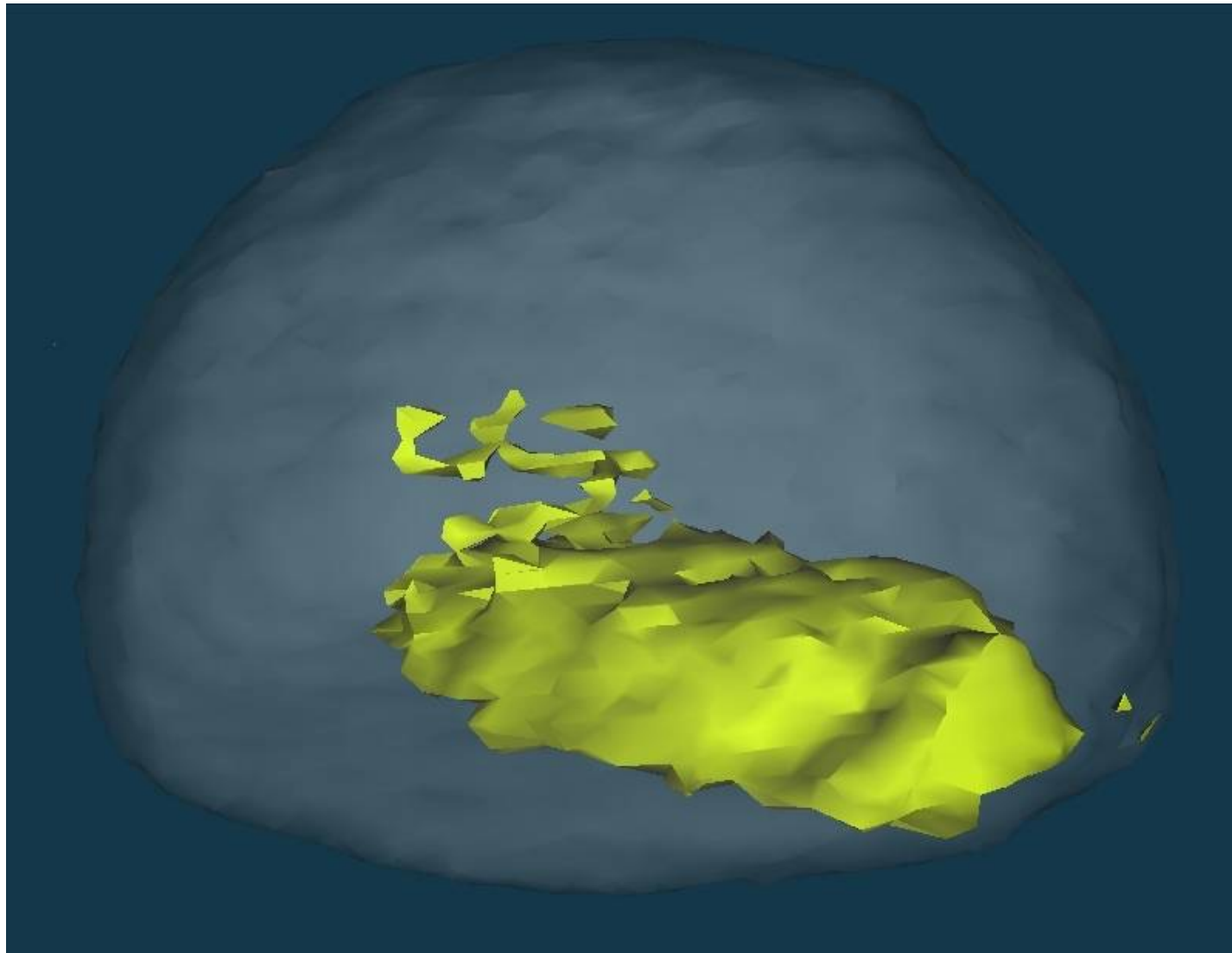


Thurmer K, Williams E, Reutt-Robey J  
Science **297** 2033 (2002)

# Density distribution across surface

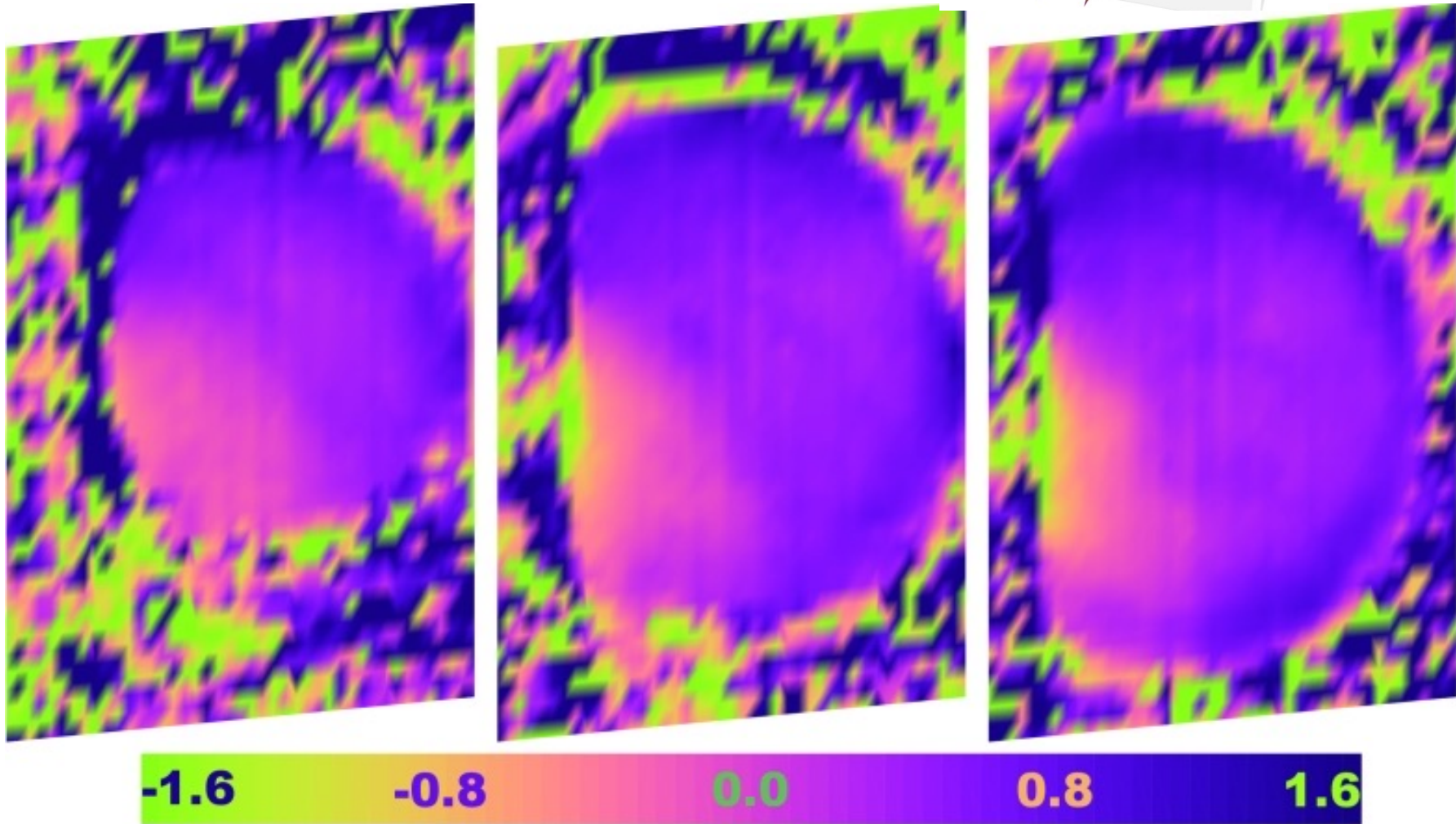
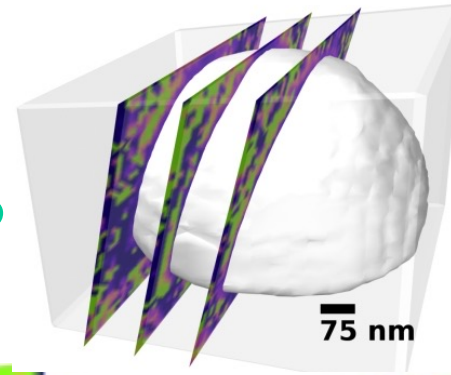


# Modeling of 3D Phase Bump

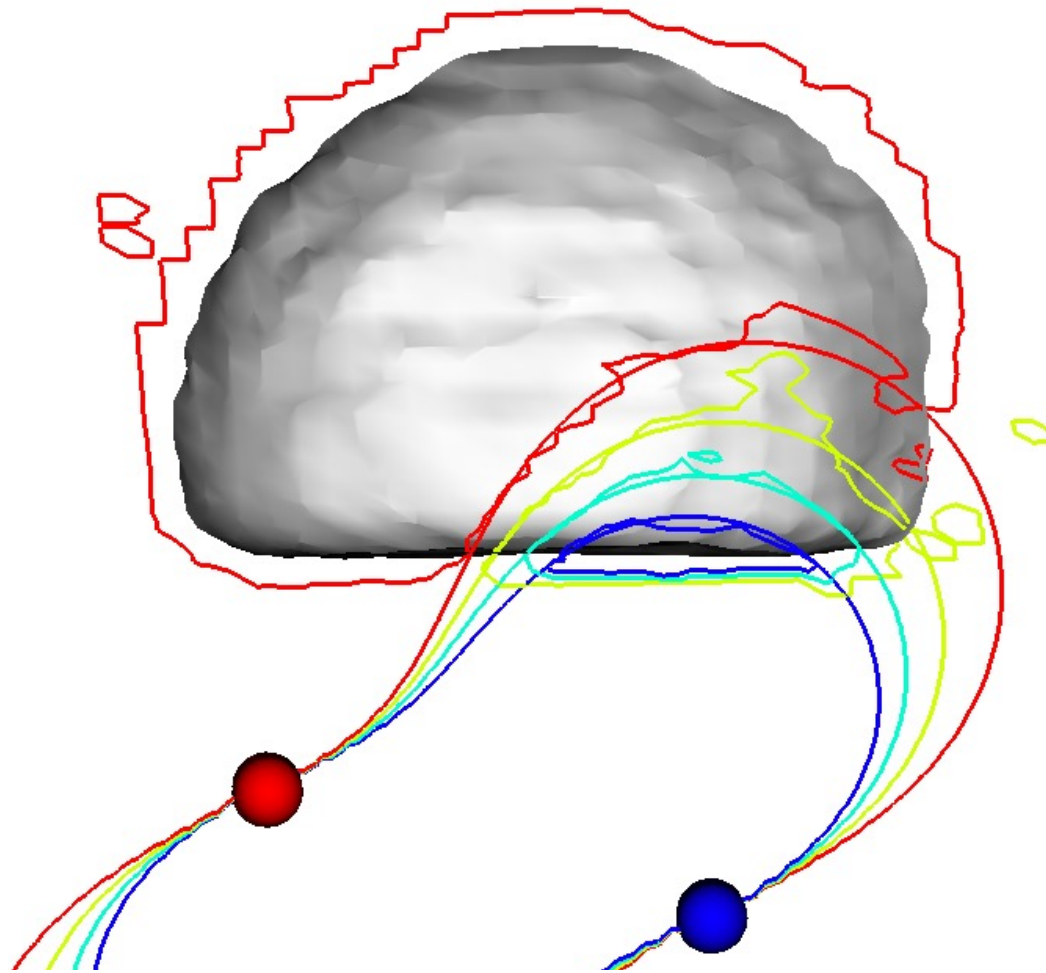


I. K. Robinson iNANO School

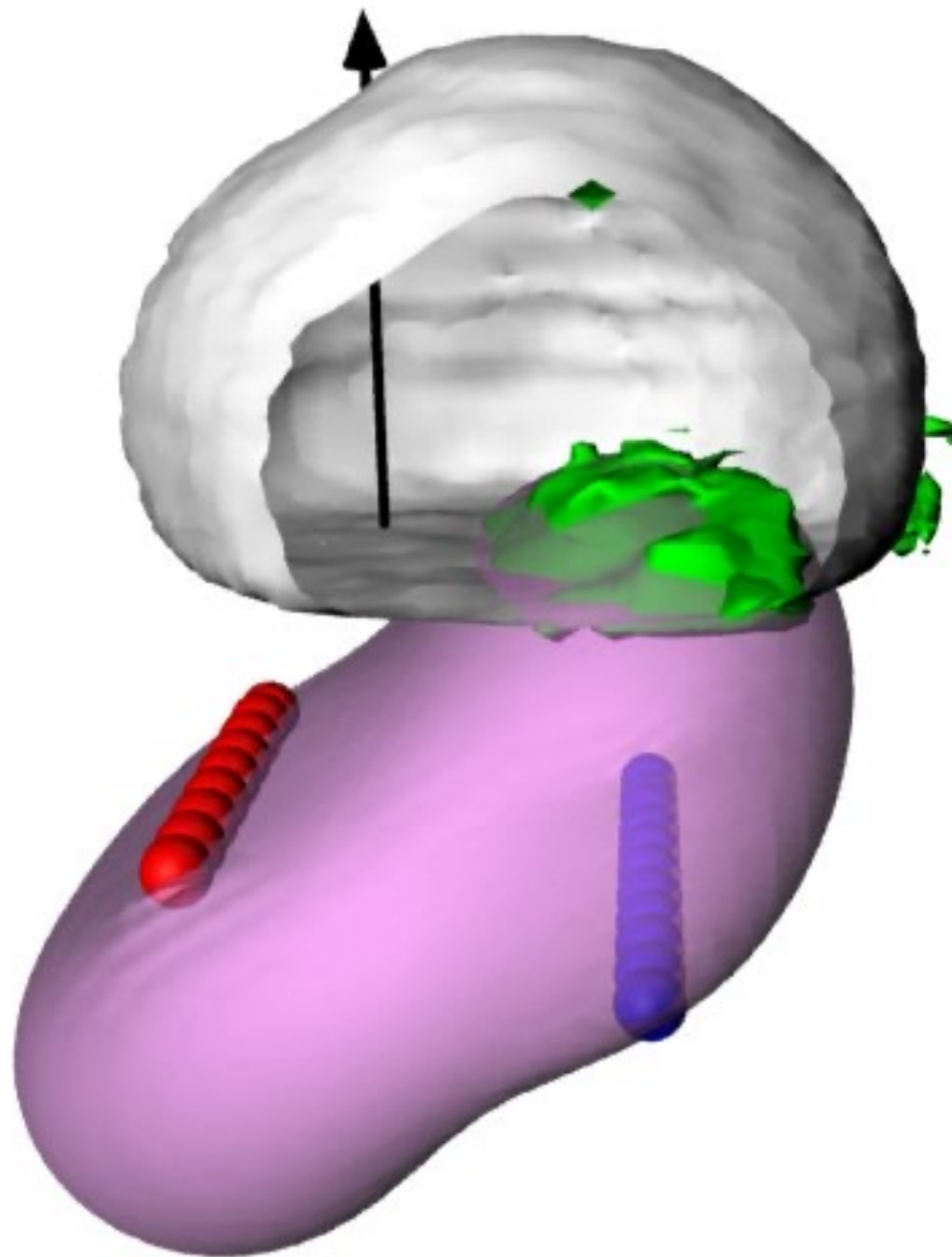
# 3D phase map sections



# Field lines of Point Charges



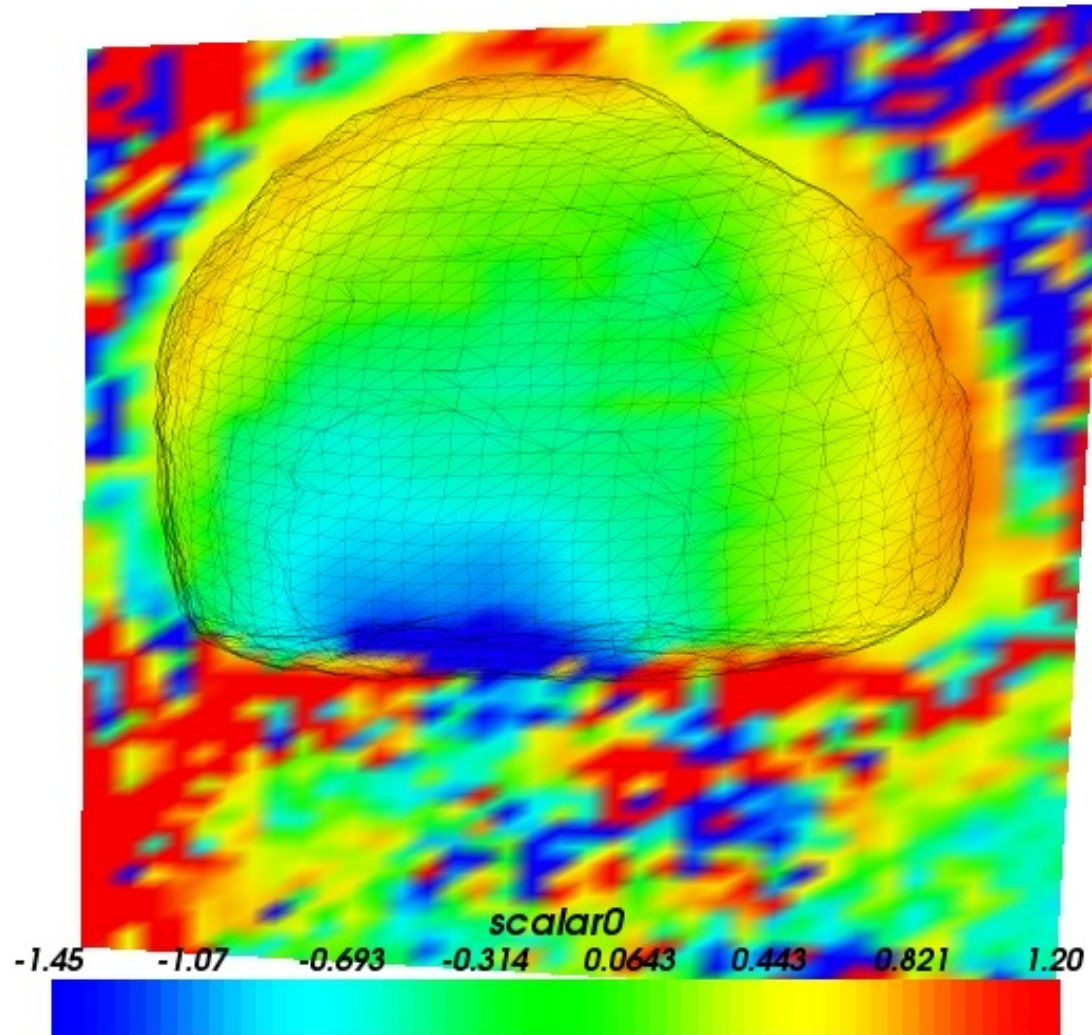
I. K. Robinson iNANO School



I. K. Robinson iNANO School

# Contours showing Positive Phase

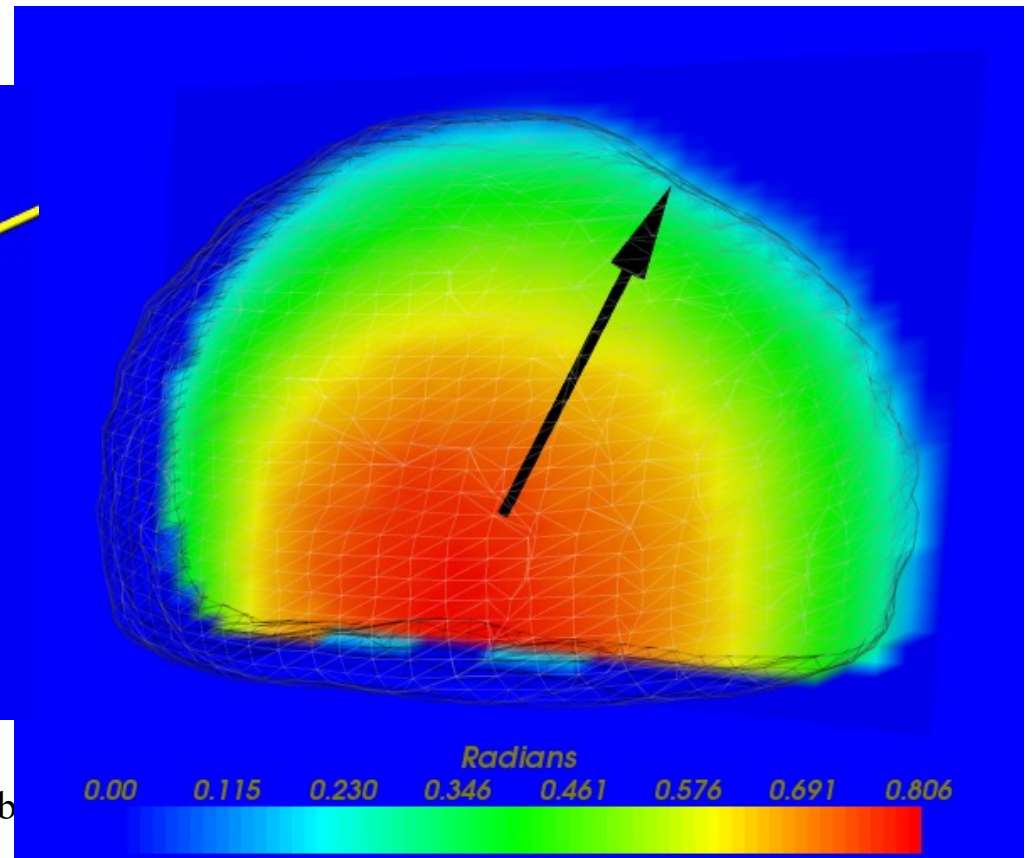
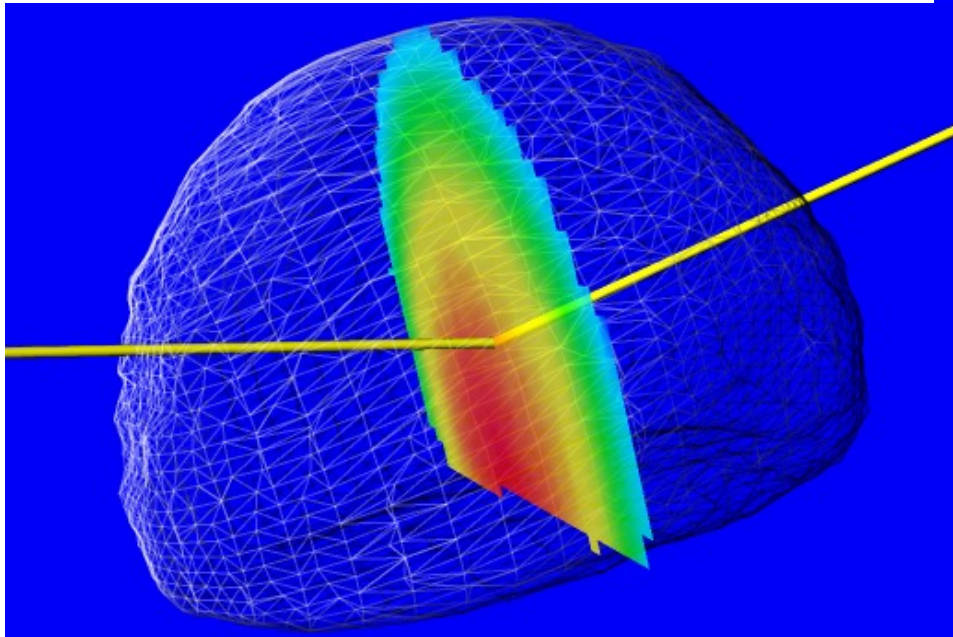
including correction for refraction by crystal



# Refraction effects in Lead at 8.9keV

Phase accumulation due to refraction along scattering path  
 $n=1-\delta+i\beta$

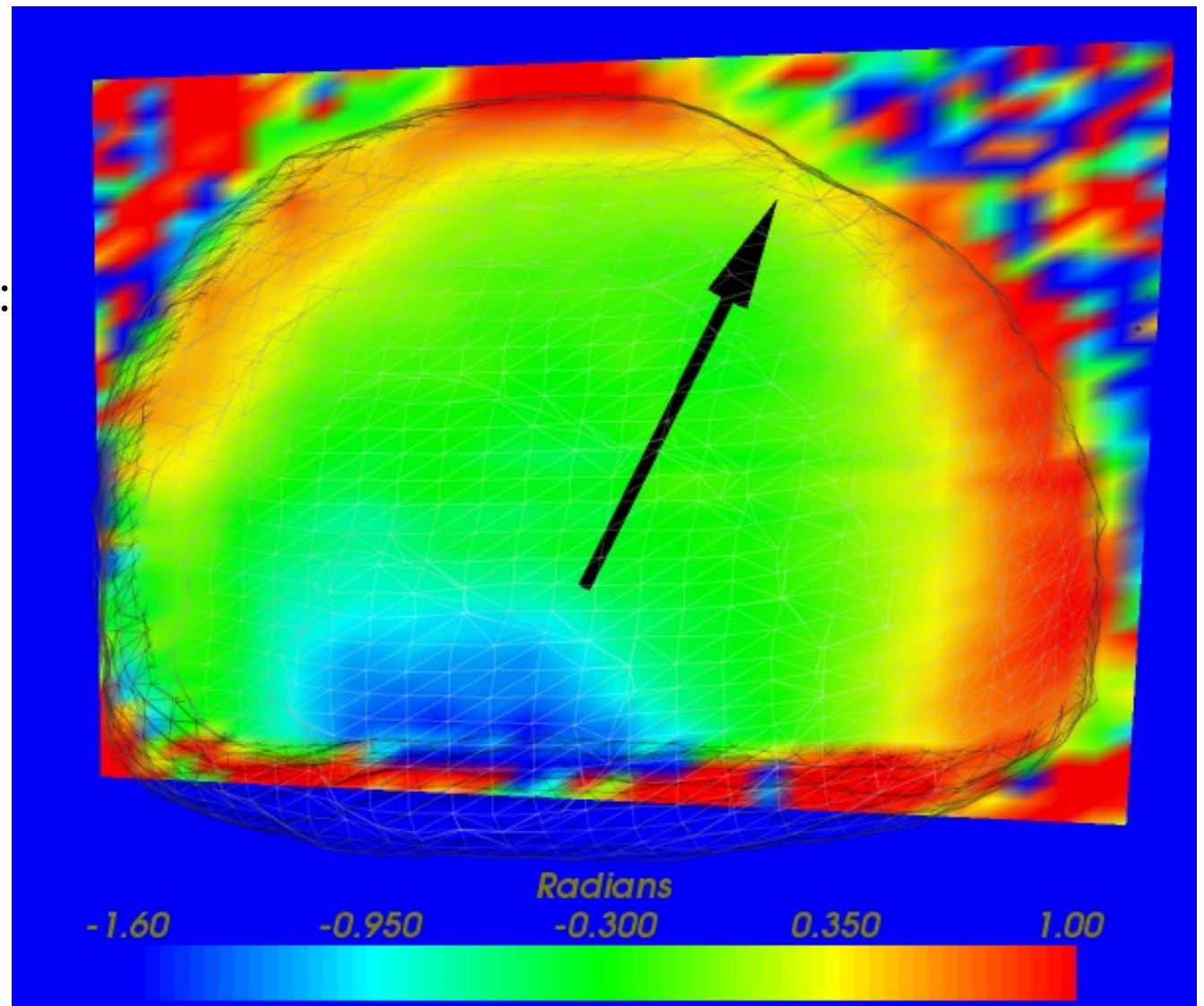
$$\delta=2.23\times 10^{-5}$$
$$\beta=2.19\times 10^{-6}$$



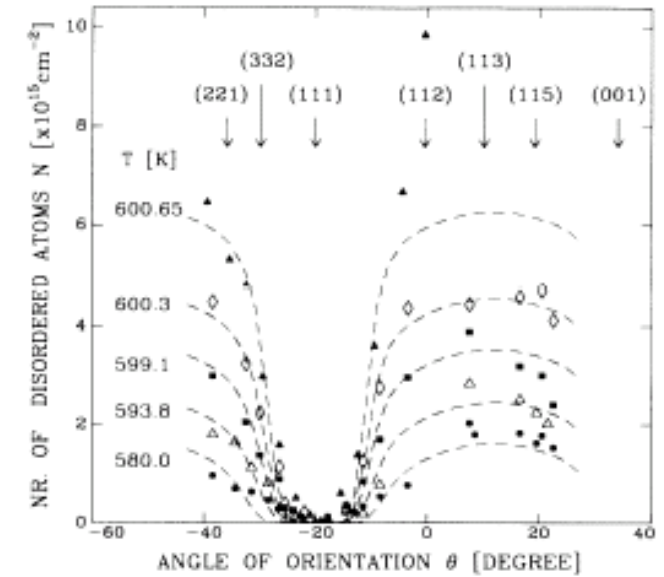
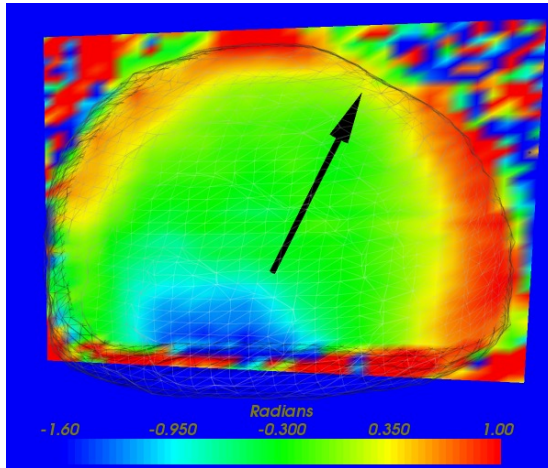
# Refraction corrected phase map

Max phase = 1.15rad  
= 0.052nm

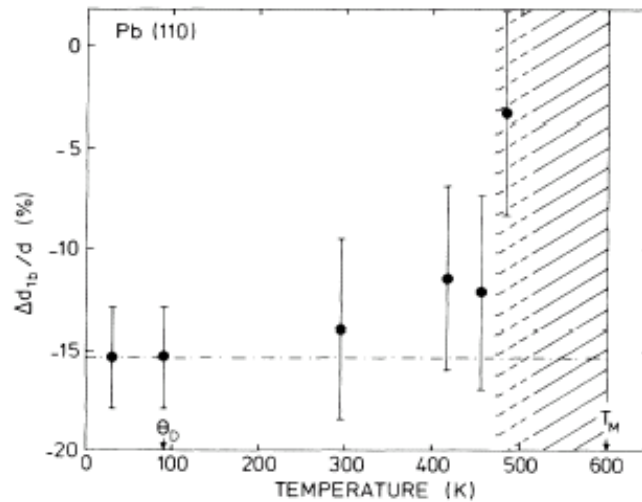
Phase on the (111) facet:  
= 0.47 rad  
= 0.02nm



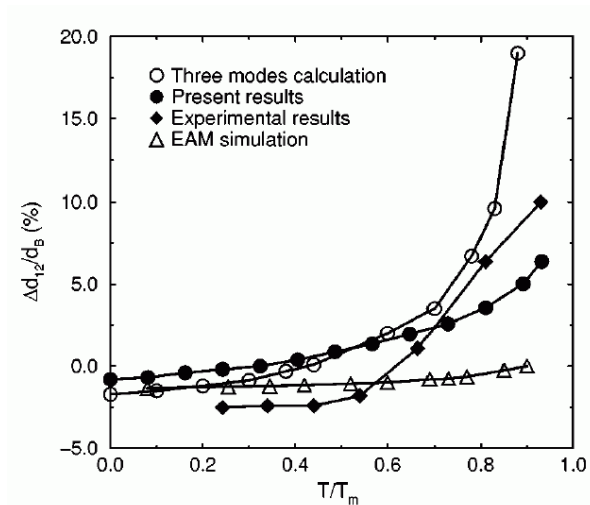
# “Anomalous” Thermal Expansion (of Surfaces)



Pluis, van der Gon, Frenken, van der Veen  
PRL 59 401(1987)



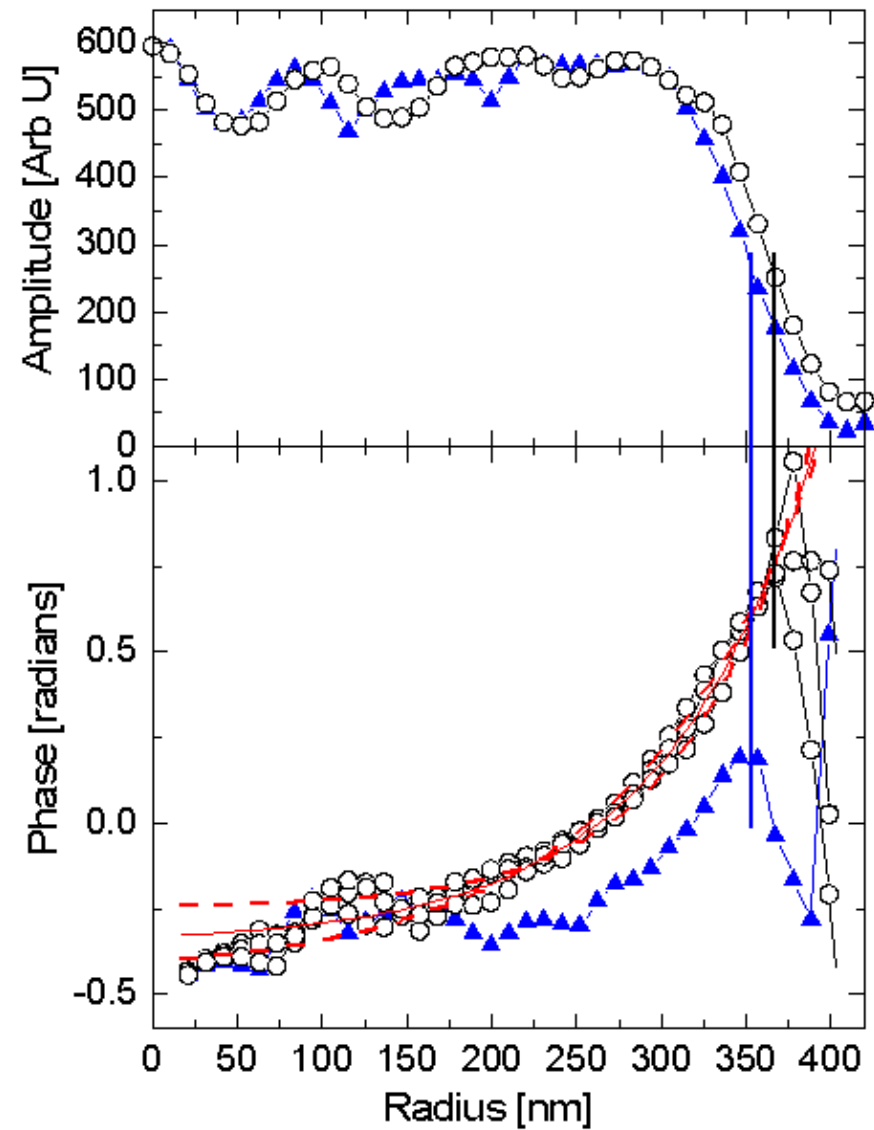
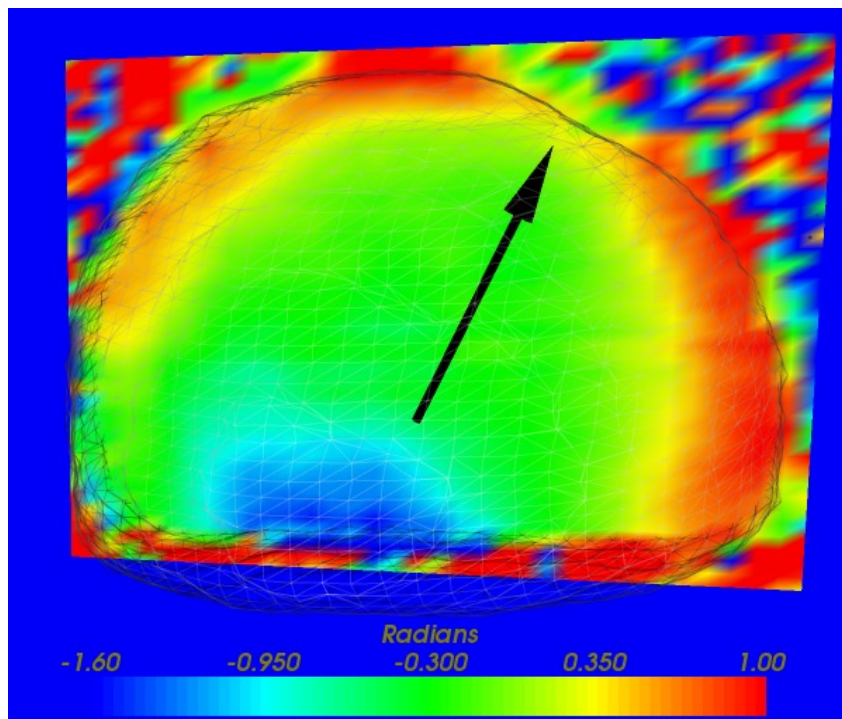
Frenken, Huusen, van der Veen  
PRL 58 (1987)



I. K. Robinson iNANO S Ag(111) theory J. Xie (Scheffler group)  
PRB 59 970 (1999)

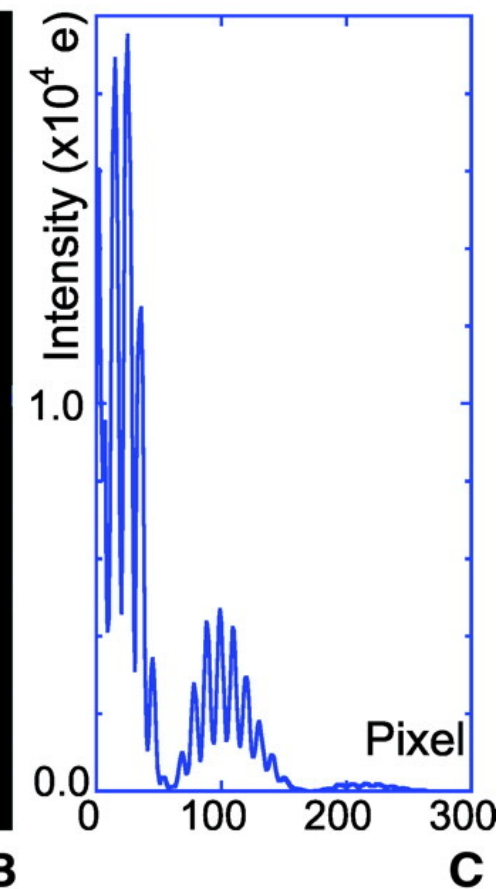
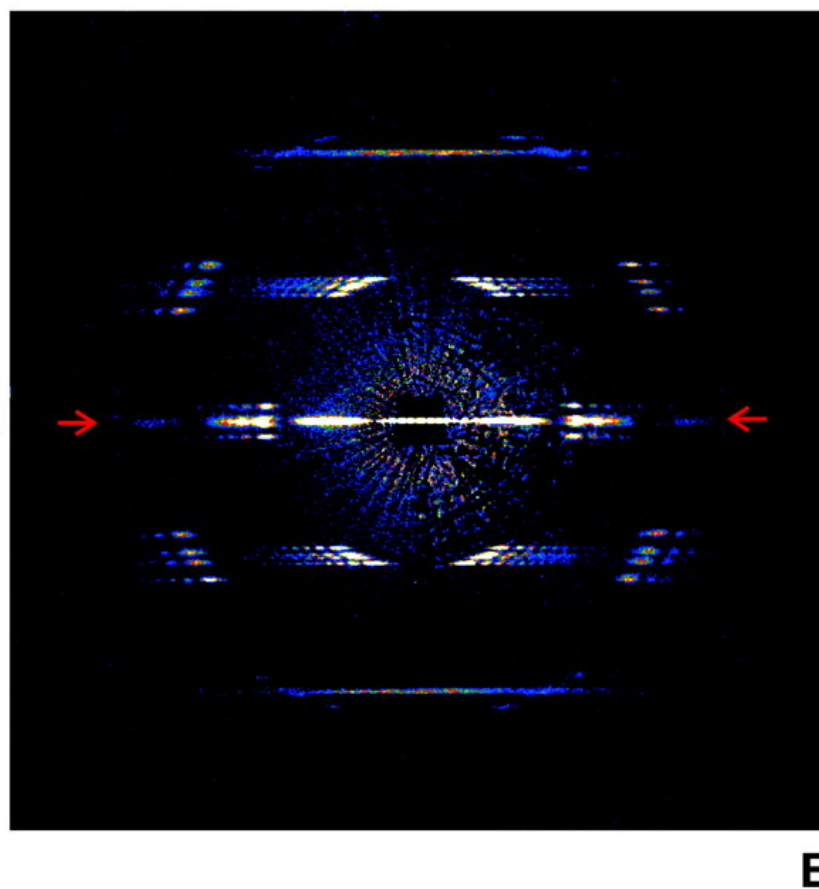
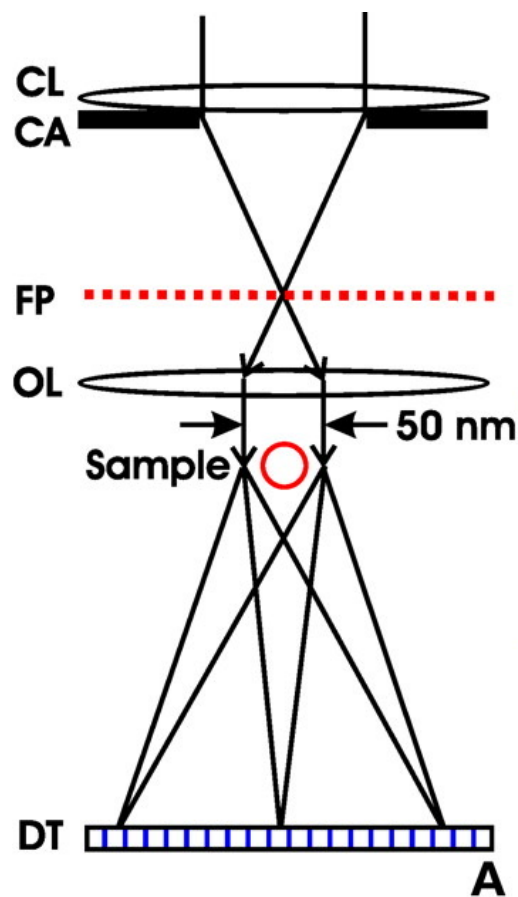
Facets subtend  $18.6\text{deg} \pm 2.6$   
ECS predicts  $14\text{deg}$

Depth measured  $90\text{nm} \pm 20$   
Expect about  $75\text{nm}$



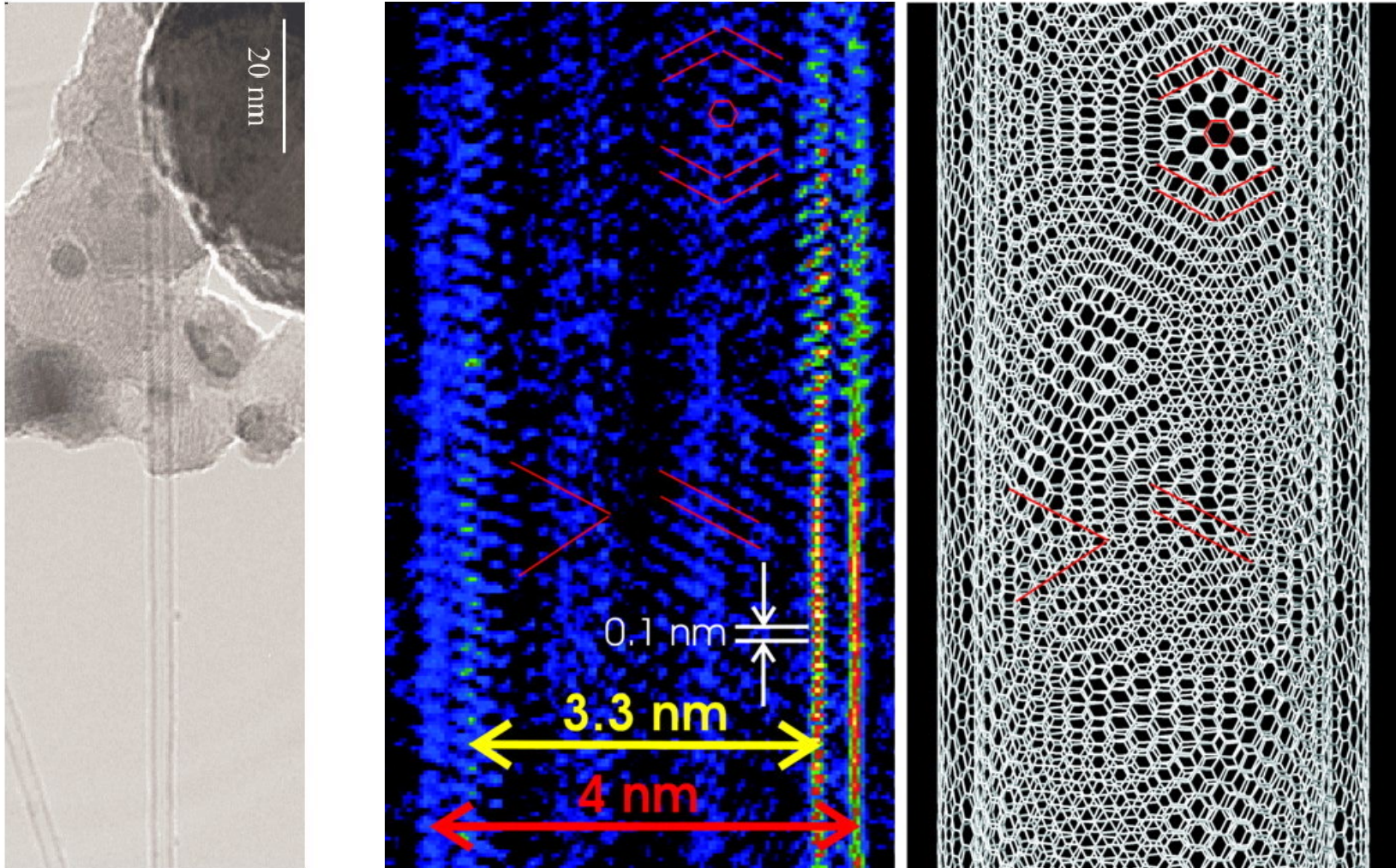
# Electron Diffraction from C-nanotube

Jim Zuo et. al. Science 300 1419 (2003)



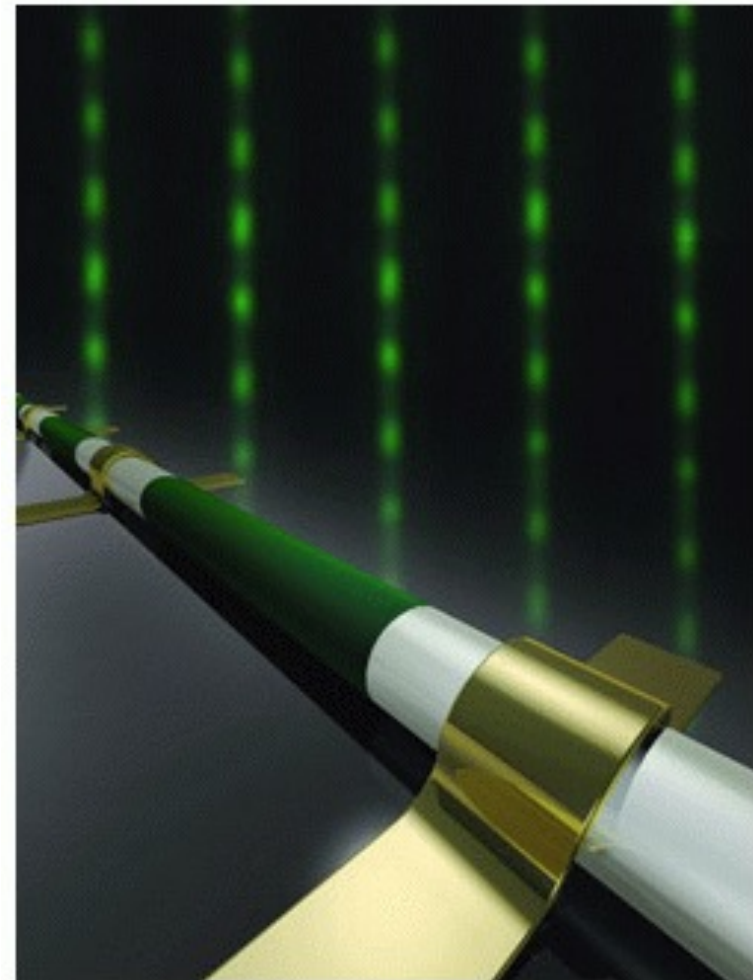
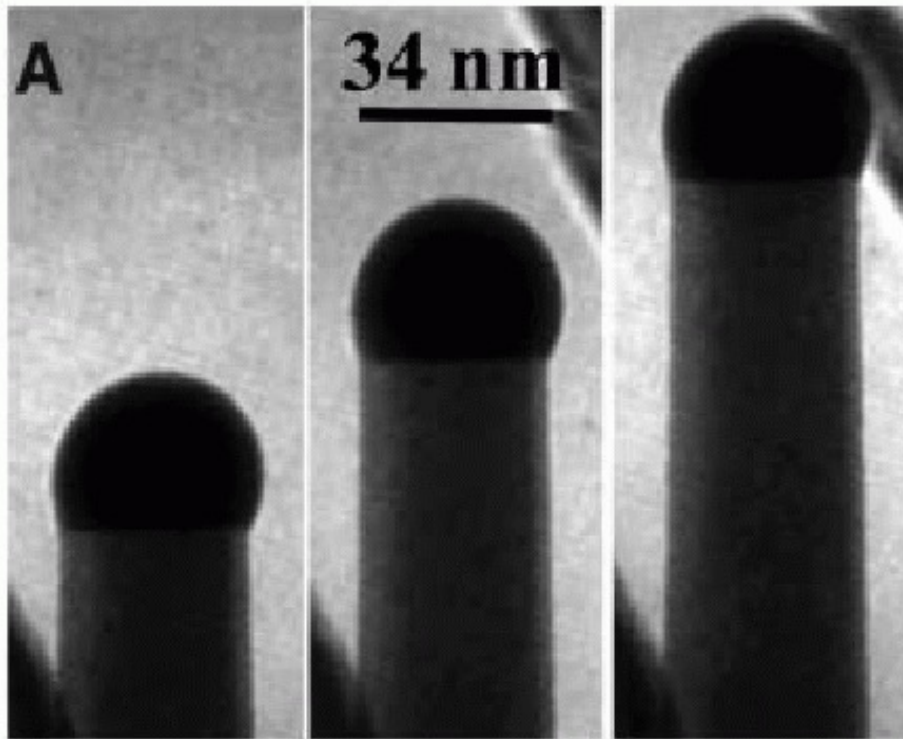
# Images of DW C-nanotube

Jim Zuo et. al. Science 300 1419 (2003)



# VLS growth of nanowires

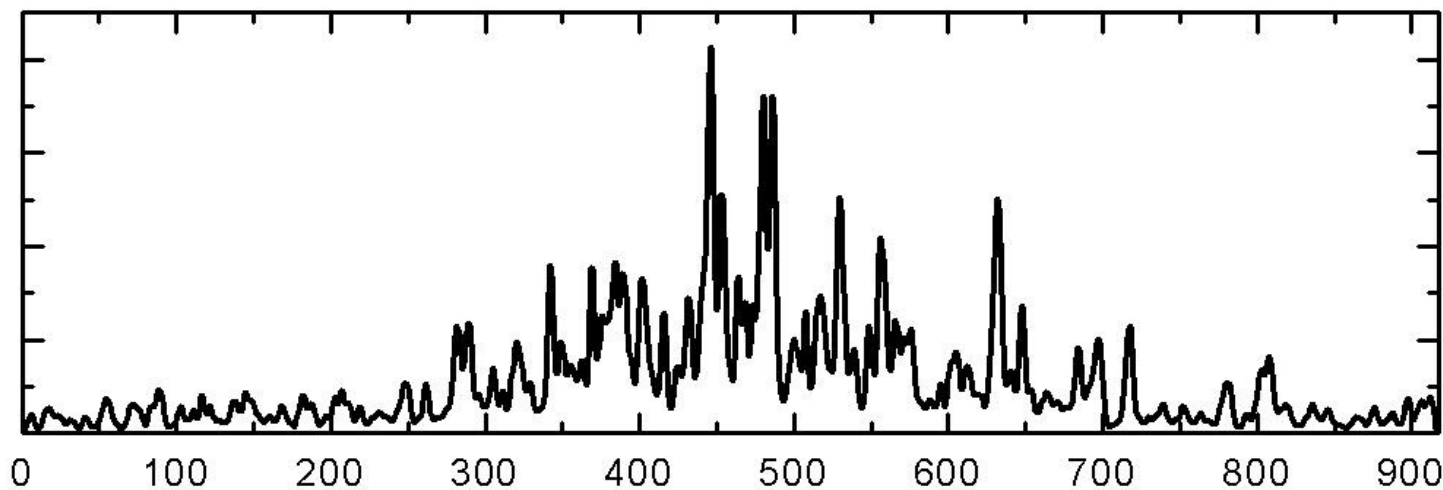
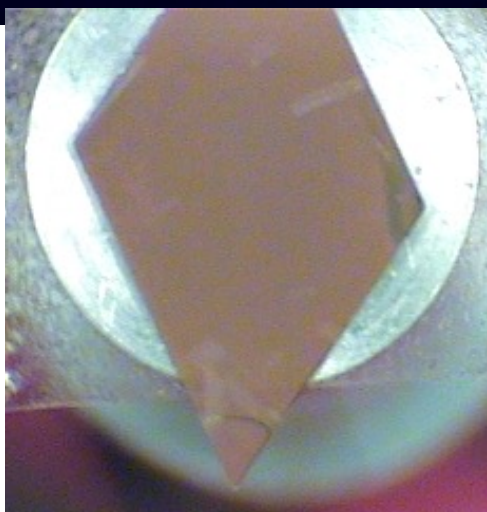
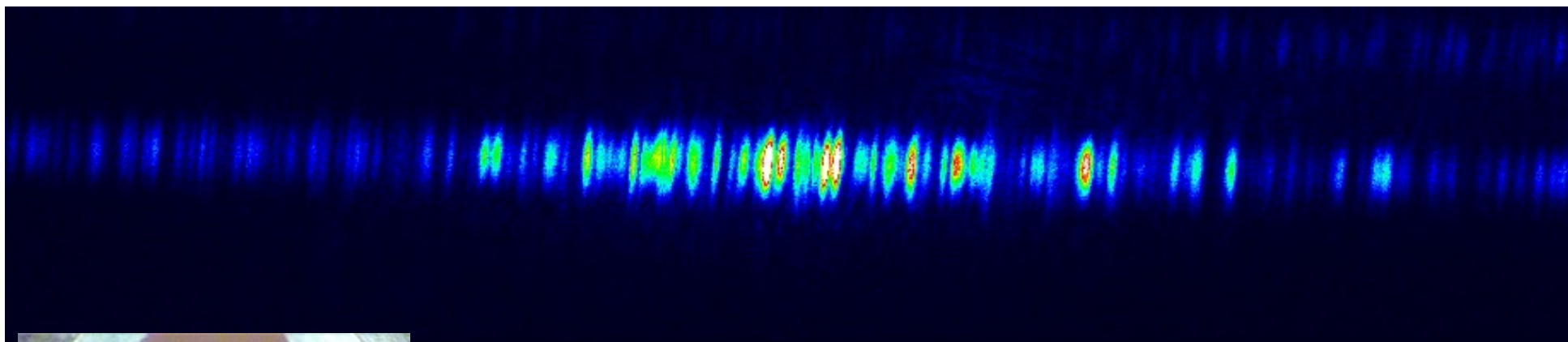
S. Kodambaka et al., *Science* 316 729 (2007)



I. K. Robinson *et al.*, NiSi/Si nanowire heterostructure devices. *Nature* **430**, 61 (2004).

# GaAs Nanowire “Barcode”

Vincent Favre-Nicolin, Joel Eymery (CEA),  
Rienk Algra (Philips), Ross Harder

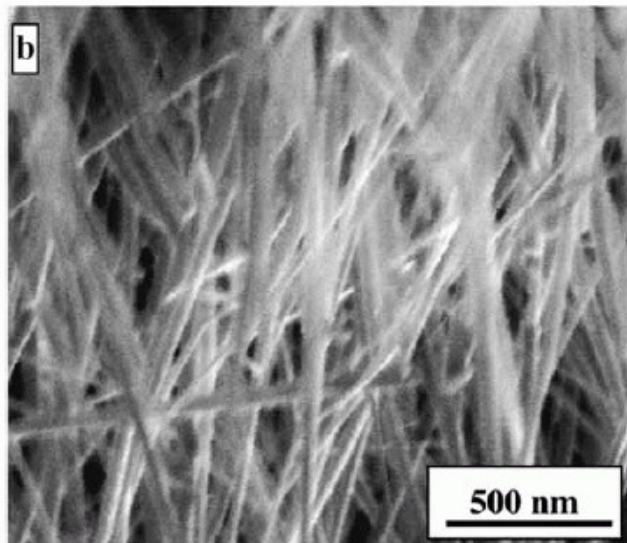
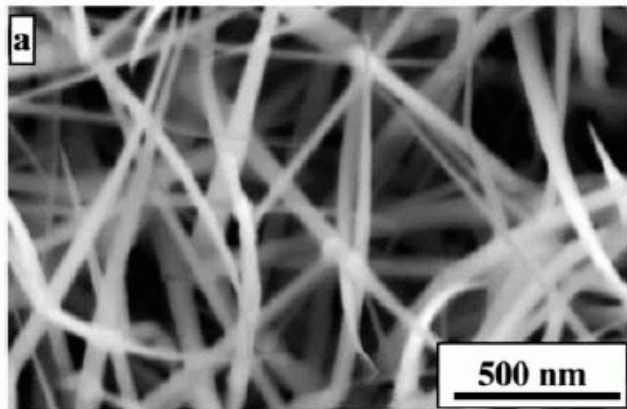


GaAsNW1106-22.spe  
B9348 from Philips

Pixel number (22.5 micron)

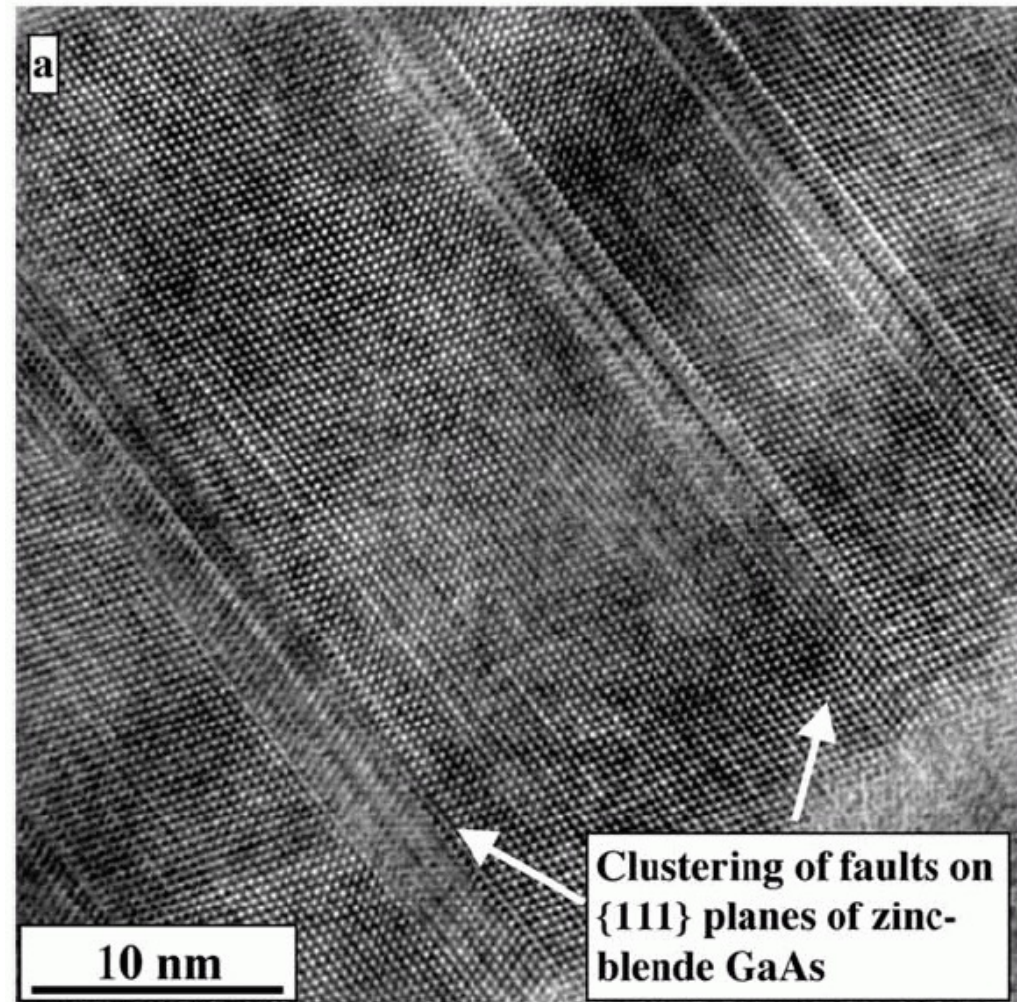
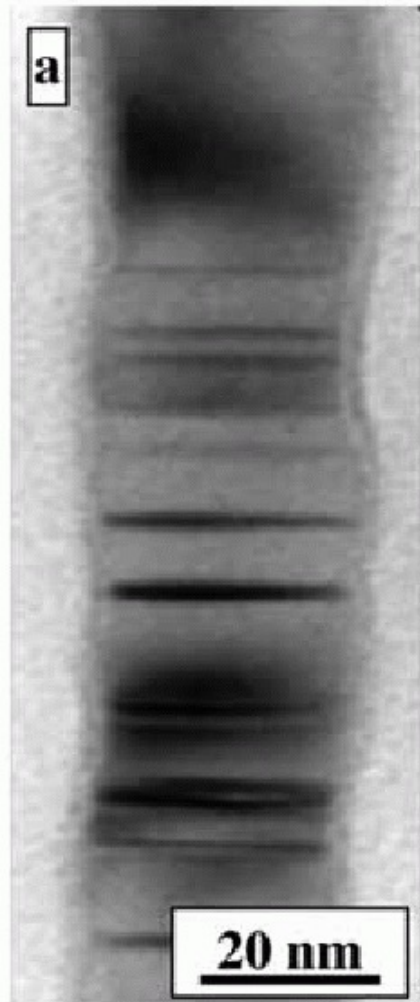
# Dark Field TEM of GaAs Nanowires

R. Banerjee et al, Phil. Mag. Lett. 86 807 (2006)



# Dark Field TEM of GaAs Nanowires

R. Banerjee et al, Phil. Mag. Lett. 86 807 (2006)

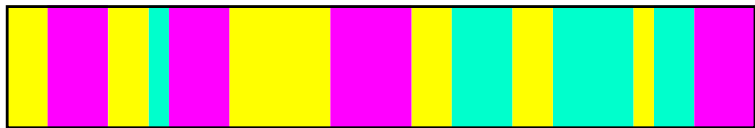


# Models of Barcode Diffraction

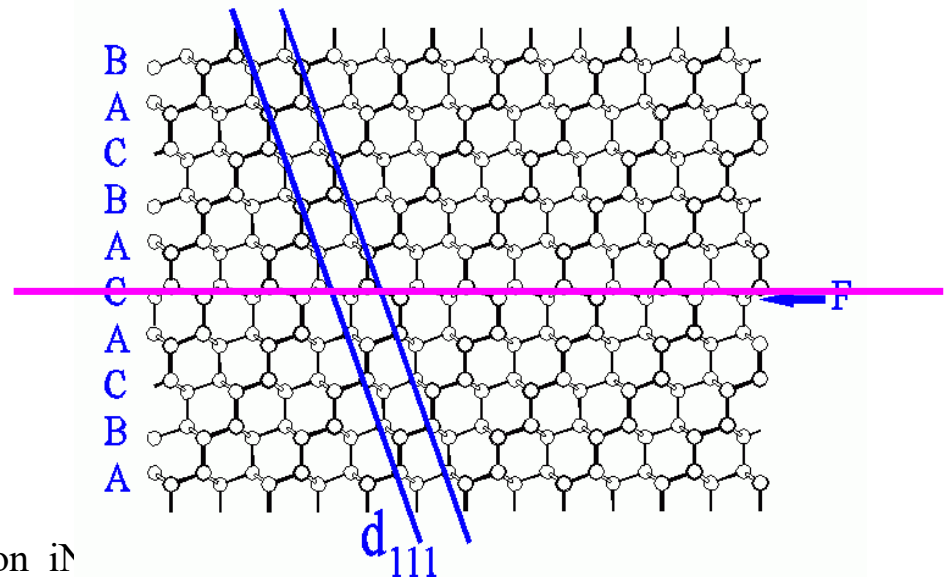
(111) wires at (11-1) reflection



- Twinned stacking sequence

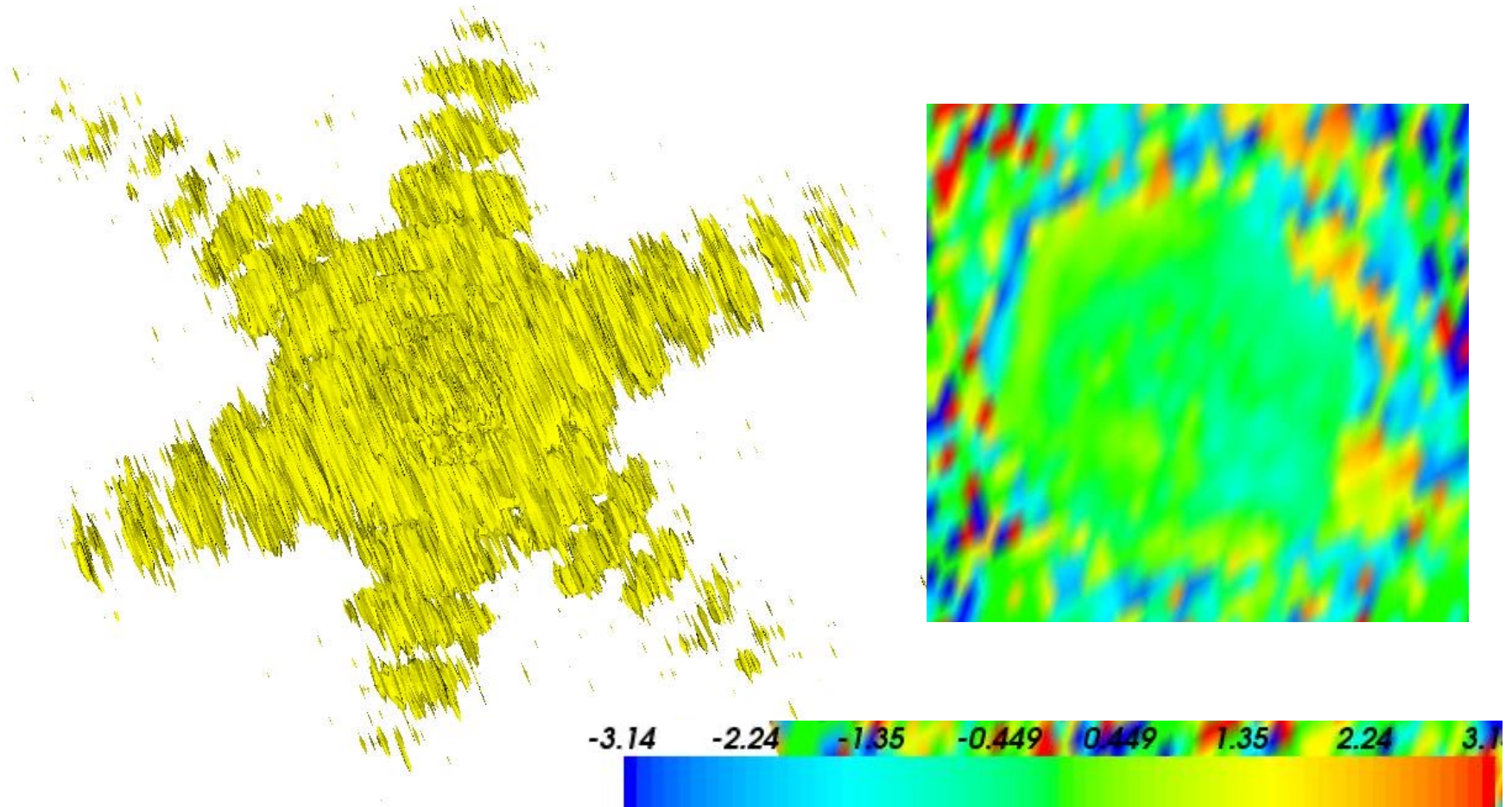


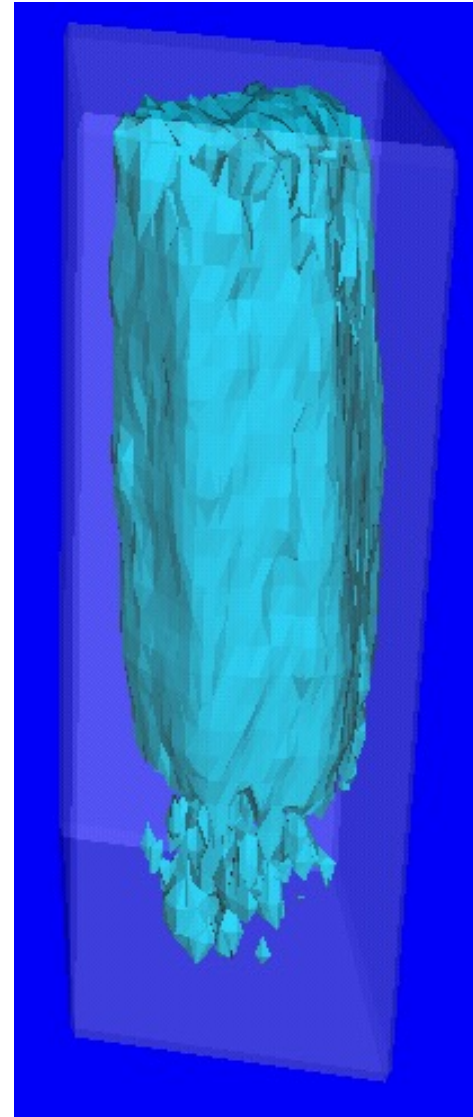
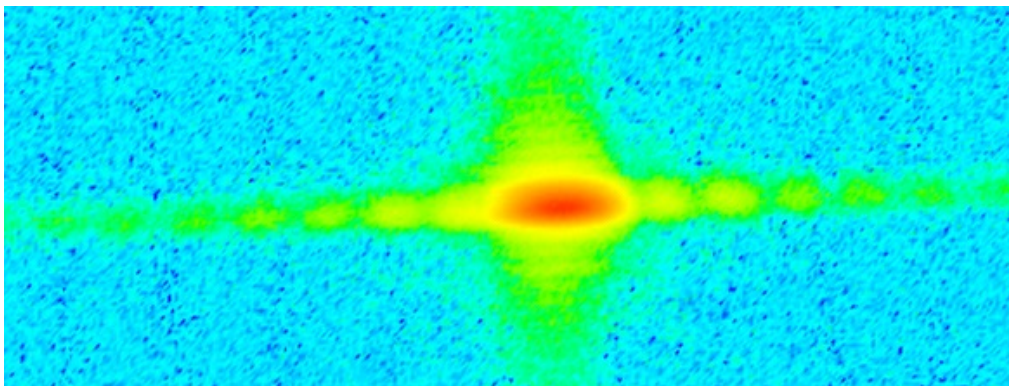
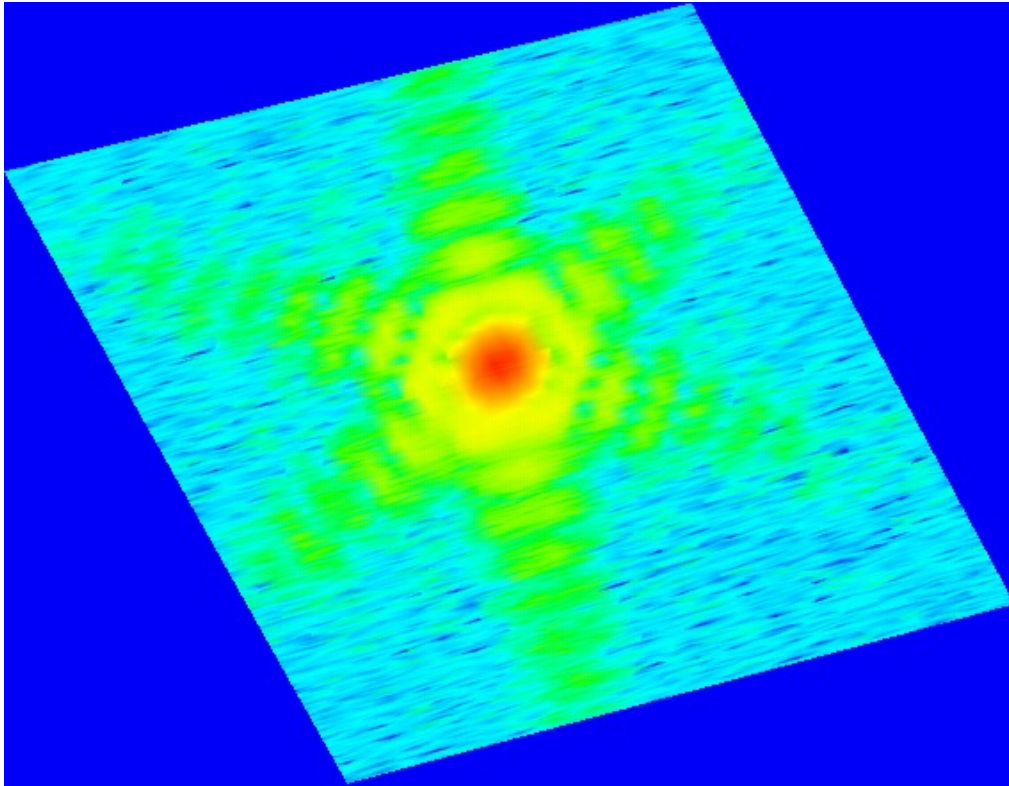
- Deformation faults



# ZnO Nanowire Reconstruction

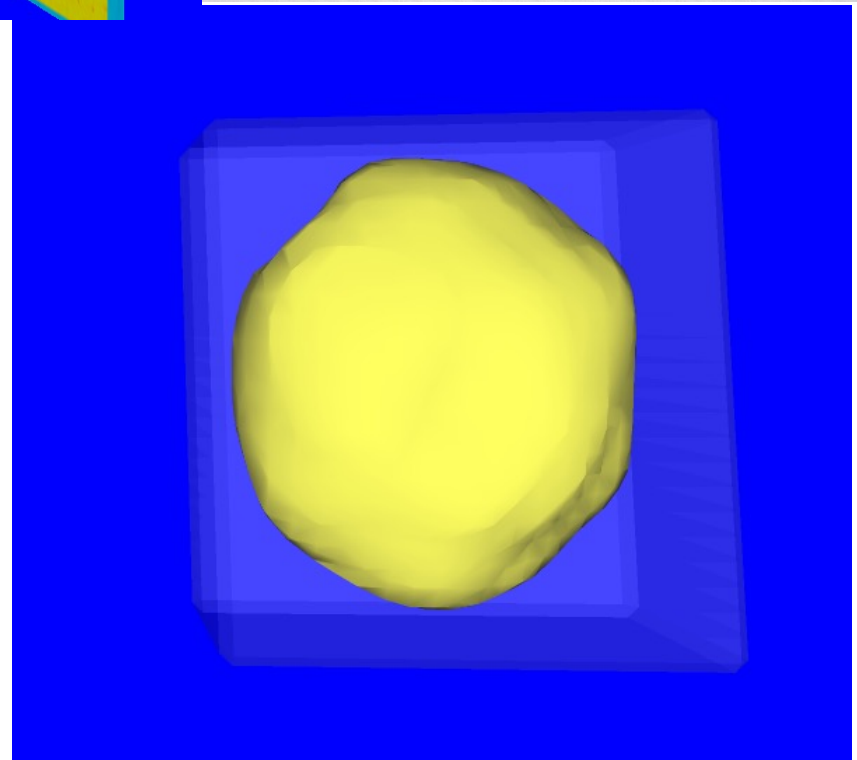
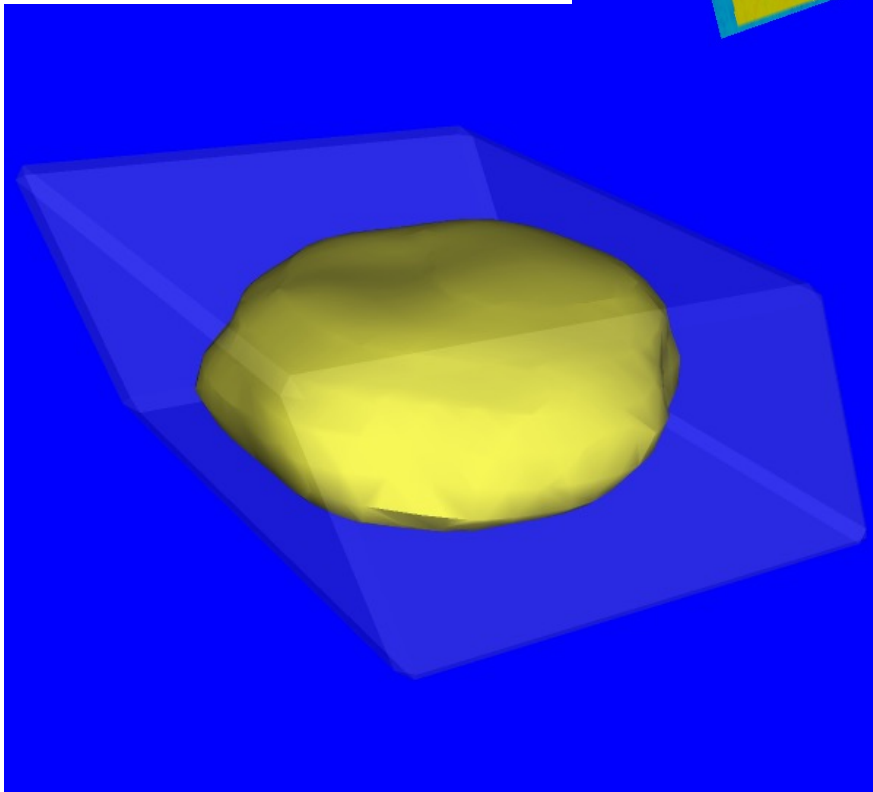
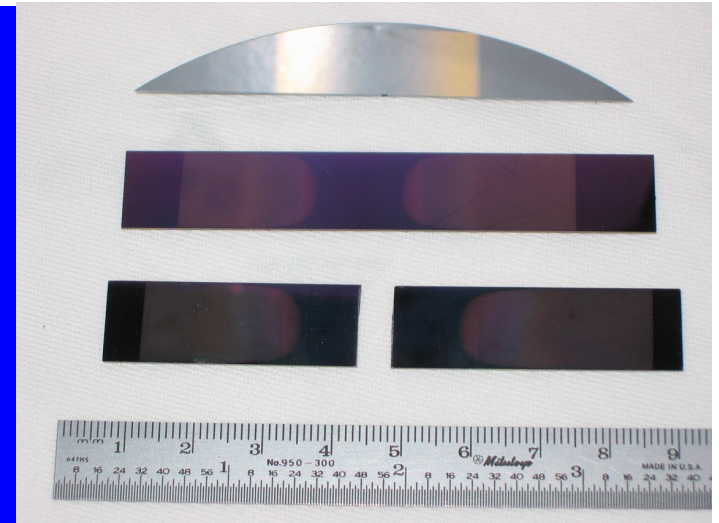
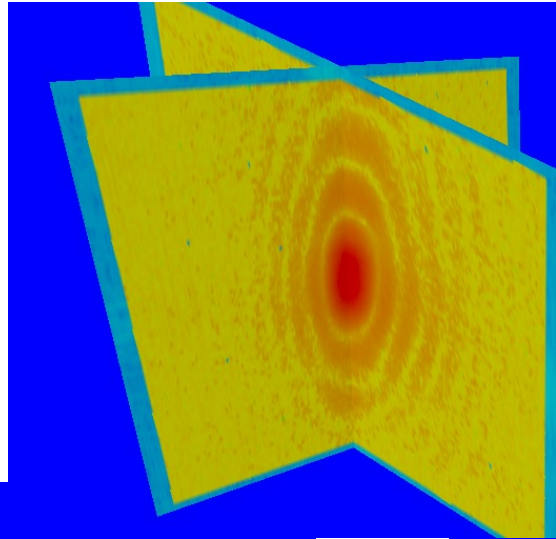
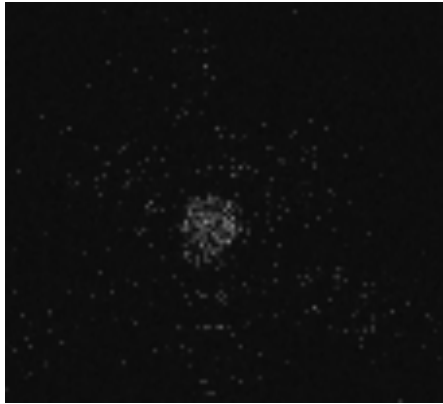
Ross Harder, Steven Leake, PhD project at UCL





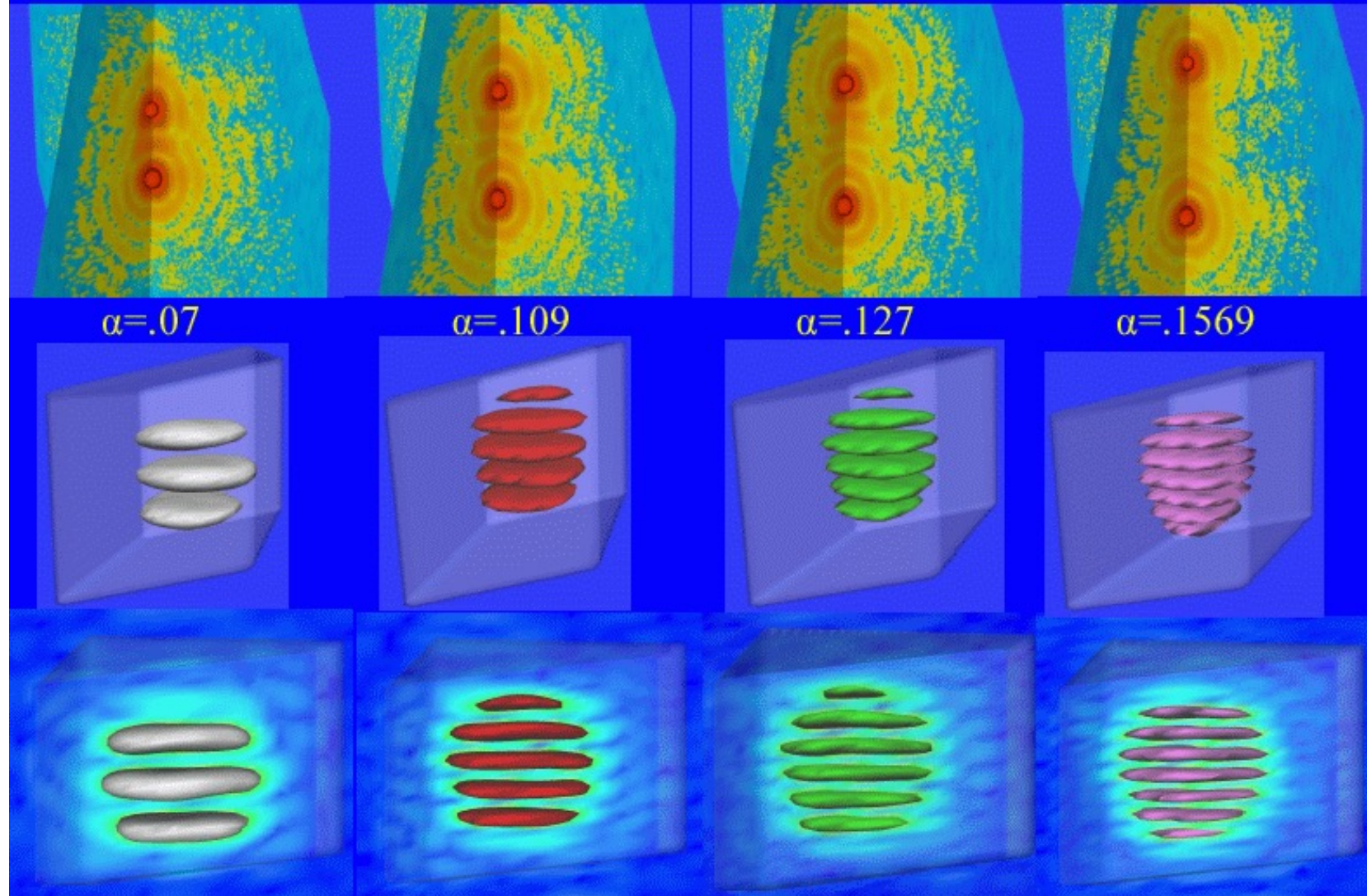
# 3D Au crystal (7/06)

XFD-OFM Chian Liu, Ali Khounsary

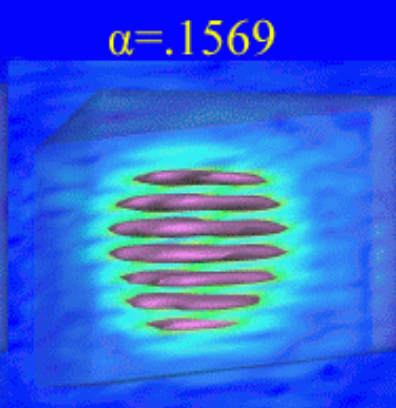
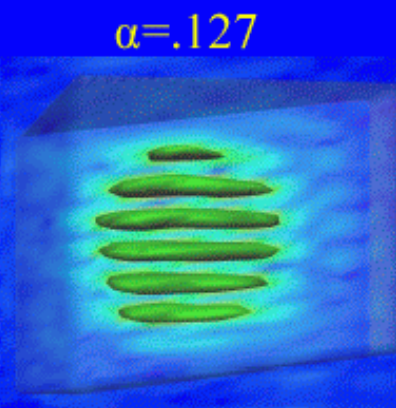
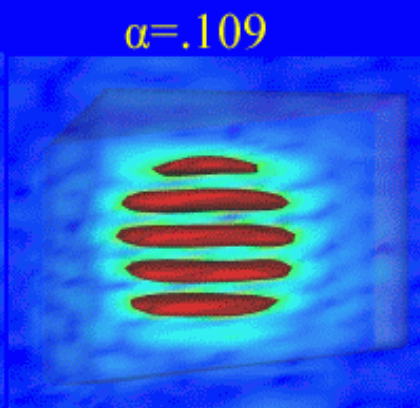
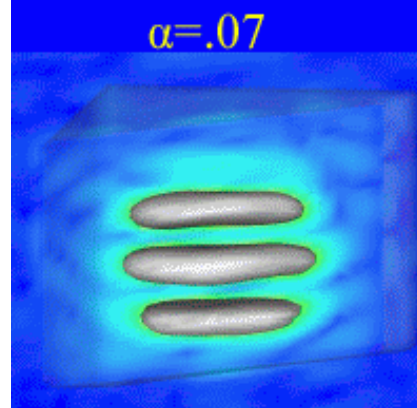
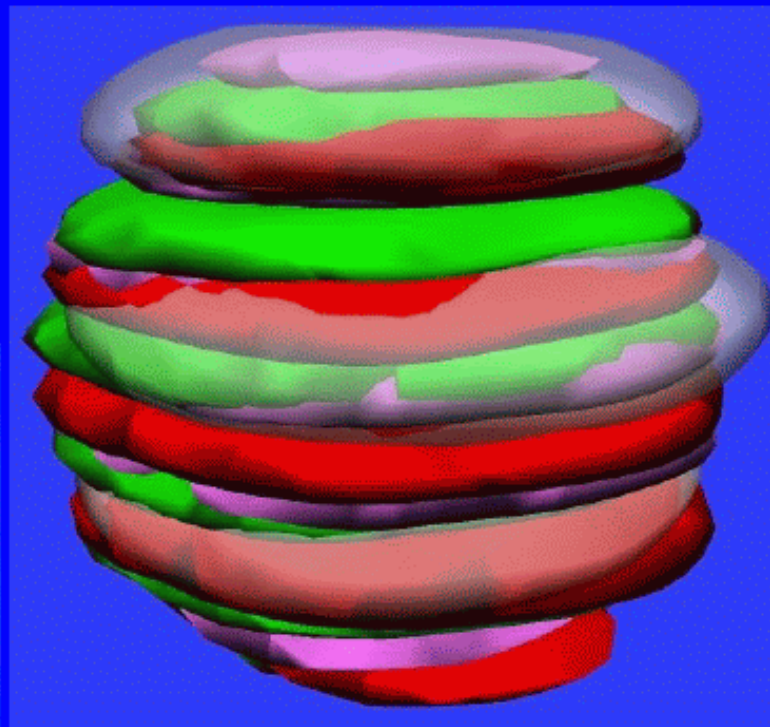
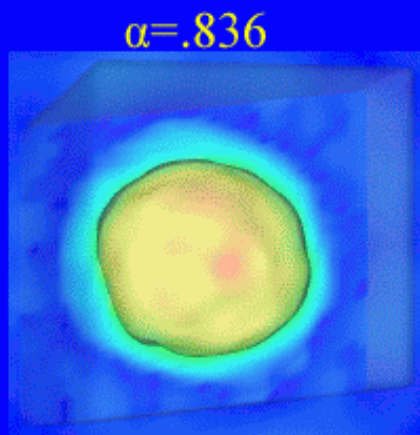
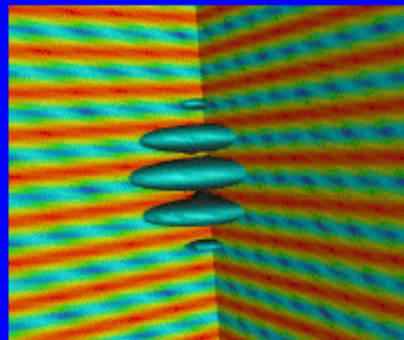


Robinson

# 3D Standing Wave Diffraction from Au



# Standing Wave Ptychography?



# Important Contributions from

Paul Fuoss

Peter Bennett

Doon Gibbs

Ben Ocko

Peter Eng

Robert Feidenhans'l

Jens Als-Nielsen

Mike Altman

Elias Vlieg

Sunny Sinha

Don Walko

Franz Himpsel

Argonne

Arizona

Brookhaven

Brookhaven

Chicago

Copenhagen

Copenhagen

HKUST

Nijmegen

San Diego

Urbana

Wisconsin

# More Important Contributions:

Ross Harder	UCL
Steven Leake	UCL
Piotr Gryko	UCL
Meng Liang	Illinois
Garth Williams	Melbourne
Mark Pfeifer	LaTrobe
Franz Pfeiffer	SLS
Ivan Vartanants	DESY

# Conclusions

- Au quantum wires on Stepped Si
- Facetting of Cu(115) seen in CTRs
- Nanocrystal: paradigm of Surface/Bulk
- Chemically synthesized Ag cubes
- Dewetting of Pb and Au hemispheres
- CVD of ZnO nanowires
- VLS growth of GaAs nanowires